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The Viscosity of Undercooled Liquid Glucose

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The viscosities of undercooled liquid glucose have been extensively studied by three very different methods. Between 145° and 80° about eighty determinations have been made by the falling sphere method; between 80° and 32° seventy-five determinations have been carried out by a concentric cylinder method; and between 34° and 22° thirty samples have been measured by a cylinder torsion method. A series of "best values," ranging from 5.6 poises at 145° to $9.1(10)^{13}$ poises at 22°C, have been tabulated from these results. They represent "true" viscosities and not plasticities. That the viscosities of the glucose depend very much upon the history of the sample and its mode of preparation has been shown by several experiments. From a consideration of the variation of the viscosity with the reciprocal of the absolute temperature some "disorientation" energy values have been derived. These are much larger than the formal heat of fusion of glucose and indicate considerable association.

INTRODUCTION

VISCOSITY is an important factor in determining whether a liquid will crystallize or form a glass on cooling. Accordingly, measurements of the viscosity of several glass-forming liquids have been a concomitant of the studies on glass which are now being carried on at Stanford University. In this paper we shall present the results of an extensive investigation of the viscosity of undercooled liquid glucose between 145° and 22°C. The determinations have been made by three different methods and cover a range of values from 4 poises up to nearly 10^{14} poises. When the viscosity approaches the latter figure, the glucose has already assumed all the superficial aspects of an isotropic, amorphous solid.

PREPARATION OF THE UNDERCOOLED LIQUID GLUCOSE

As in other studies,[1] the samples of liquid glucose were prepared by heating crystalline, anhydrous α-glucose (Pfanstiehl Chemical Company) in a flask immersed in a paraffin bath. The glucose crystals melted at about 145°C and were then maintained under a vacuum at 155°–160° for a short time, usually about five minutes, in order to eliminate bubbles of air or water vapor. When the liquid had become fairly clear, air was admitted and the sample was allowed to cool; it was usually straw-colored. Considerably longer periods of heating at 155° or above led to noticeable decomposition and a product which was dark brown in color.

MEASUREMENTS BY THE FALLING SPHERE METHOD

Above 80°C all viscosity measurements were made by the falling sphere method. The liquid glucose was placed in a special glass test-tube (2 ± 0.05 cm in diameter and 29 cm long) which was in all respects like that described by Gibson and Jacobs.[2]

[1] G. S. Parks, H. M. Huffman and F. R. Cattoir, J. Phys. Chem. **32**, 1366 (1928); G. S. Parks and W. A. Gilkey, J. Phys. Chem. **33**, 1430 (1929).

[2] W. H. Gibson and L. M. Jacobs, J. Chem. Soc. **117**, 473 (1920). See also E. Mack and W. G. France, *A Laboratory Manual of Elementary Physical Chemistry*, Van Nostrand Co., New York (1928), pp. 64–69.

Commercial ball-bearings served as spheres. Three sizes (1/8 inch, 3/32 inch and 1/16 inch diameters) were used. Each ball-bearing was measured with a micrometer and only those which would involve an error of 0.5 percent or less were retained. In the case of the 1/16 inch (0.1588 cm) balls, which were used in sixty per-cent of the determinations, an independent measurement of the average diameter by displacement with water yielded 0.1593 cm as a result. The density of the steel in these balls was found to be 7.66 g per cm³ at room temperature.

A Pyrex jar (10 cm in diameter and 40 cm long), which was jacketed with "85 percent magnesia" and fitted with a cork cover, served as a small adjustable thermostat for the measurements. It was filled with a light oil and equipped with a stirrer and an electric heating coil. Its temperatures were measured to $\pm 0.02°$ with a mercury thermometer, graduated to 0.1° and calibrated by the United States Bureau of Standards. The viscometer containing the glucose was suspended in the center of this thermostat through a hole in the cork cover.

Windows were cut in the "85 percent magnesia," through which the etched rings on the viscometer tube could be seen. The time, t, for the fall of the ballbearings between two rings 15 cm apart was determined by a stopwatch. From this value the viscosity, η, was then calculated by the formula

$$\eta = K(d_1 - d_2)t \qquad (1)$$

where d_1 is the density of the steel spheres and d_2 is that of the liquid glucose. For the temperatures involved d_2 was estimated from the data of Parks, Huffman and Cattoir;[1a] it varied from 1.45 g per cm³ at 145° to 1.49 at 80°. K, the viscometer constant, was evaluated by the Ladenburg formula[3] from the dimensions of the apparatus. As a check upon the accuracy of the viscosity values obtained in this manner, we next measured the viscosity of refined castor oil and of anhydrous glycerol. The result obtained for castor oil, 12.7 poises at 18°C, is 8.9 percent above that reported by Kahlbaum and Räber.[4] Our result for glycerol, 14.3 poises at 20°, is 2.7 percent below that recently found by Ley and Kirchner.[5] Such checks are really very satisfactory in view of the character of these two liquids.

Viscosity measurements between 80° and 145°C were next made by this method upon eight different samples of glucose. In all about eighty different values were determined and for purposes of brevity these have been represented graphically in Fig. 1, where the logarithm of the viscosity has been plotted against temperature.

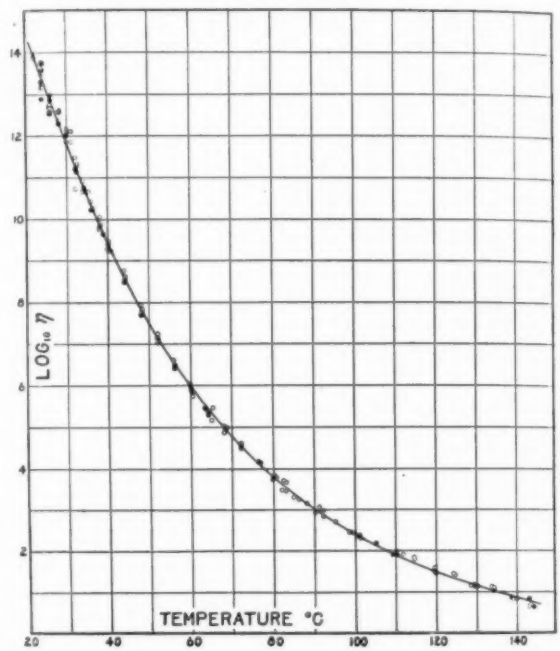

FIG. 1. A plot of the experimentally determined viscosity values for undercooled liquid glucose. The circles represent individual values; the heavy dots represent two or more values which practically coincide.

Differences in the values at any particular temperature are primarily due to the individuality of the different glucose samples and not to a lack of reproducibility in the viscometer itself.

MEASUREMENTS BY THE CONCENTRIC CYLINDER METHOD

Viscosity measurements between 80° and 32°C were made by a concentric cylinder viscometer which was a modification of that used previously

[3] R. Ladenburg, Ann. d. Physik **22**, 287 (1907). See also reference 2.

[4] G. W. A. Kahlbaum and S. Räber, Abd. Kais. Leop.-Carol Deut. Akad. d. Naturf. Halle **84**, 203 (1905); also quoted by W. H. Herschel, U. S. Bur. Stand. Tech. Paper **112**, 24 (1919).

[5] H. Ley and U. Kirchner, Zeits. f. anorg. Chemie **173**, 395 (1928).

by Parks and Gilkey.[1] The outer cylinder, containing the glucose, consisted of a stout Pyrex test-tube (2.2 cm internal diameter) which was tightly clamped to a special steel stand and was thus held stationary. A hollow steel rod (0.98 cm in diameter and 30 cm long) served as the inner, rotating cylinder. This rod rotated in a pair of bearings which were attached to the steel viscometer stand at suitable distances above the Pyrex test-tube. These bearings, together with a collar on the rod, held it in a central, vertical position in the test-tube and maintained a constant depth of immersion (about 7 cm) in the liquid glucose. A wheel of known dimensions was mounted on the rod above the top bearing and served to produce a suitable rotating moment by means of a weight that was attached to a fine cord wound around the wheel and suspended over a pulley. A small counterweight was used to overcome friction in the bearings. The lower end of the rod was welded shut, and then carefully turned and mounted so that it revolved in a true manner.

A 3-liter Dewar jar, filled with water, served as a small adjustable thermostat. The jar was arranged so that the surface of the water was about 2 cm below the top of the outer cylinder of the viscometer and a like distance above the surface of the glucose sample. A cork cover was made for the jar in order to reduce heat losses; it had openings for the inner cylinder, a stirrer and an electric heating coil. The temperature of this water bath was measured to 0.01° by a calibrated mercury thermometer, graduated to 0.1°. The temperature of the glucose immediately adjacent to the inner steel cylinder was also measured by means of a 4-junction copper-constantan thermocouple, which could be inserted to the bottom of this hollow tube. In preliminary tests of the apparatus it was found that the thermocouple in such a position registered between 1° and 3° lower than the bath temperature, the loss of heat along the steel rod being responsible for this temperature gradient. Accordingly, in order to eliminate this heat loss, a small electric heating coil was mounted on the bottom of the lower bearing and surrounding the inner cylinder at this point. By adjusting the current through this coil, the entire viscometer system could be maintained at a uniform, constant temperature.

The rate of rotation was measured by observing the time necessary for one revolution, or a definite fraction of a revolution, of the inner cylinder. A small mirror was fixed on this inner cylinder between the two bearings, and a curved galvanometer scale with a telescope at its middle point was mounted at a distance of about 50 cm from the mirror. This scale was carefully calibrated in radians so that small rotations could be measured with accuracy. The time required for a given amount of rotation was determined with a stopwatch and in every case a check run was immediately made to insure consistent time measurements. For low viscosities complete revolutions were measured, while small fractions of a revolution were used for the highest values observed.

From this time measurement and the known dimensions of the apparatus the viscosity was calculated by the formula

$$\eta = C(R_2^2 - R_1^2)/4\pi\omega(l_1+l_2)R_1^2R_2^2, \qquad (2)$$

where C is the moment of force producing the rotation of the steel cylinder, ω is the resulting angular velocity, R_1 is the outside radius of the steel cylinder, R_2 is the inside radius of the Pyrex tube, l_1 is the actual depth of immersion of the inner cylinder in the glucose, and l_2 is a correction factor to provide for the viscous effect on the bottom. The value of l_2 was determined by preliminary experiments with different depths of immersion of the inner cylinder; it amounted to about one percent of l_1.

With this instrument viscosity measurements were made upon nine different samples of glucose. A total of about seventy-five values were determined and these are now represented graphically in Fig. 1.

Measurements by the Twisted Cylinder Method

At 32°C undercooled liquid glucose has assumed all the superficial aspects of a solid and below this temperature it was found impractical to carry on viscosity determinations by the concentric cylinder method. However, between 34° and 22° we did succeed in making measurements upon small cylinders of the glucose by the

method which has been previously described by Trouton and Andrews.[6]

These glucose cylinders were prepared by pouring the liquid into special brass molds at 100° and then slowly cooling the material to about 35°, at which temperature removal of the samples from the molds became feasible. Two sizes were employed: (1) between 34° and 24° cylinders of 0.83 cm diameter and 2.54 cm length; and (2) at 24° and 22° cylinders of 0.53 cm diameter and 2.60 cm length. In the casting process small knobs were formed at each end of the cylinders for fastening them into the socket clamps of the viscometer.

During a viscosity determination a glucose cylinder thus formed was held vertically in a special apparatus which maintained the lower knob of the cylinder stationary and rotated the upper knob very slowly by means of a torque provided by a simple system of weights and pulleys. The angular rotation thereby produced was measured on polar coordinate paper fastened on a wheel which revolved on the same shaft as the upper knob of the glucose sample. The times required for suitable rotations varied from fifteen minutes up to as much as ten hours, depending upon the temperature of the measurements. The viscosity of the glucose was calculated by the formula

$$\eta = 2Cl/\pi r^4\omega, \qquad (3)$$

where C is the torque applied, r and l are, respectively, the radius and length of the cylinder, and ω is the angular velocity of the upper end relative to the lower.

In order to maintain a constant temperature in the glucose sample during such a viscosity measurement, the viscometer was placed inside a large wooden box which was provided with a glass door in front and otherwise thermally insulated. By means of a fan, a thermoregulator and an electric heating coil within this box temperatures could then be maintained constant to $\pm 0.1°$.

With this method a total of more than seventy viscosity determinations were made upon thirty different glucose cylinders. Some typical values thereby obtained are represented graphically in Fig. 1, where this method has yielded all the results below 31° and about half of those at 32° and 34°. From the range of values found at any one temperature it is evident that the viscosity of the undercooled glucose in this region is very sensitive to small variations in the conditions incidental to its preparation. Moreover, as we shall later show, there was a noticeable tendency for the viscosity of any particular cylinder to increase on successive days. Accordingly all these measurements represented in Fig. 1 were made upon cylinders within a few hours of their preparation.

Below 25° these glucose samples assumed the brittleness of a glass and therefore a question arose as to the existence of torsional elasticity in the material. However, an appreciable elastic return on the removal of the applied torque, although it was looked for, was noted in no case; and a study, which is being carried on at present in our laboratory by Mr. John Reagh, now shows that under the conditions existing in the twisting of these glucose cylinders the elastic effects must have been relatively unimportant.

A Table of Best Values

The viscosity values obtained by these three, very different methods are in excellent agreement, as can be readily seen from the plotted results in Fig. 1. At 80° and 32°, where there was an actual overlapping of the methods, the

Table I. *Viscosity data for undercooled glucose.*

Temp. °C	Viscosity, η (in poises)	$\text{Log}_{10}\eta$	Temp. °C	Viscosity, η (in poises)	$\text{Log}_{10}\eta$
22.0	9.1×10^{13}	13.96	75.0	2.0×10^{4}	4.29
24.0	2.6 "	13.41	80.0	6.6×10^{3}	3.82
26.0	7.3×10^{12}	12.86	85.0	2.5 "	3.40
28.0	2.2 "	12.34	90.0	1.05 "	3.02
30.0	6.6×10^{11}	11.82	95.0	4.9×10^{2}	2.69
32.0	2.1 "	11.32	100.0	2.5 "	2.40
34.0	6.8×10^{10}	10.83	105.0	1.41 "	2.15
36.0	2.2 "	10.35	110.0	8.0×10	1.90
38.0	7.8×10^{9}	9.89	115.0	5.0 "	1.70
40.0	2.8 "	9.44	120.0	3.2 "	1.50
45.0	2.5×10^{8}	8.40	125.0	2.1 "	1.32
50.0	3.0×10^{7}	7.48	130.0	1.45 "	1.16
55.0	4.7×10^{6}	6.67	135.0	1.03 "	1.01
60.0	9.3×10^{5}	5.97	140.0	7.6	0.88
65.0	2.2 "	5.35	145.0	5.6	0.75
70.0	6.3×10^{4}	4.80			

[6] F. T. Trouton and E. S. Andrews, Proc. Phys. Soc. London **19**, 47 (1909).

differences between the various results were clearly due to the individuality of the samples used rather than to the particular method of measurement. The smooth curve drawn through the experimental data represents, in our judgment, the best values for undercooled liquid glucose over the temperature range of this study. These viscosity data are also recorded in Table I.

Very early in the course of the present investigation the question arose as to whether we were dealing with true viscosity or with plasticity as the temperatures approached the region of the glassy state. To answer this question the rate of rotation of the inner cylinder in our concentric

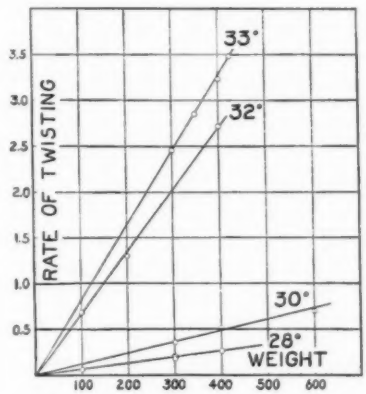

FIG. 2. The *rate of twist* of some glucose cylinders in degrees per minute plotted against the *weight* used in producing the twisting torque.

cylinder viscometer was determined for a series of different torques with a sample of undercooled liquid glucose which was maintained successively at temperatures of 52°, 49°, 47°, 40°, 37° and 35°. Likewise, the rates of twist of glucose cylinders were measured at 33°, 32°, 30° and 28°, respectively, with three or more different weights used to produce the twisting torques. For each temperature the rates of rotation, or of twist, were then plotted against the corresponding torques, as in Fig. 2. In all cases the data gave a straight line passing through the origin. Thus it is evident that we were dealing at these temperatures with true viscosity rather than with plasticity, as in the latter event these straight lines would have cut the X-axis at some distance to the right of the origin.[7]

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DEPENDENCE OF VISCOSITY UPON HISTORY

Throughout this investigation it was very evident that the viscosity of the glucose depended considerably upon the thermal history of the material and its mode of preparation.

Thus, for example, early in our work a series of measurements by the falling sphere method was made upon one glucose sample with temperatures decreasing from 138° to 86° and this was followed by a series with the temperatures increasing from the latter point up to 145°. The viscosity value at 130° in the first series of determinations was 13.5 poises; that obtained at 130° in the second series (on the following day) was 11.5 poises.

This result led to a more elaborate test of the effect of maintaining the glucose at a moderately elevated temperature for several days. In this test a sample of liquid glucose was prepared and its viscosity was first measured at 100°. It was then maintained at 67° for 24 hours, after which interval the viscosity was again measured at 100°. This procedure was repeated on the third and fourth days, but the appearance of crystals on the fifth day ended the test. The data thus obtained are given in Table II. From these results it is

TABLE II. *Effect of heating at 67°C on glucose viscosity at 100°.*

Hours of heating at 67°	Time for falling sphere in seconds	η at 100° (in poises)
0	384.3	182.7
24	378.8	180.1
48	374.1	177.8
72	369.9	175.9

evident that even at a temperature as low as 67° the viscosity of this glucose is undergoing a decided decrease with time. Two explanations for such a phenomenon can be suggested. One is that the glucose is slowly decomposing at this temperature with the formation of a little water and a consequent reduction in the viscosity of the liquid. The second is that some change in the relative amounts of the alpha, beta and, perhaps, other glucose forms present in the undercooled liquid is taking place preparatory to the formation of crystals and that this change is accompanied by a decrease in the measured viscosity. We plan to investigate this problem further.

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32.0	2.1 "	11.32	100.0	2.5 "	2.40
34.0	6.8×10^{10}	10.83	105.0	1.41 "	2.15
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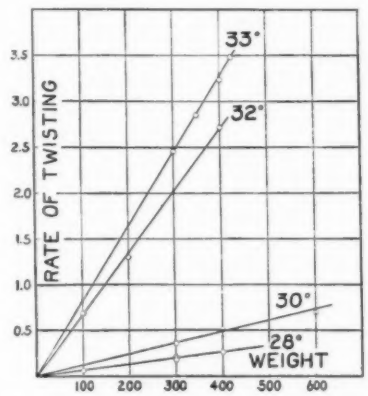

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On the other hand, at temperatures below 32° there was a noticeable increase with time in the viscosities of all our glucose samples. This phenomenon is well illustrated by the data given in Table III. A cylinder of glucose was prepared

TABLE III. *Effect of age upon the viscosity of glucose at 30°.*

Age of glucose cylinder (in days)	η at 30°C (in poises)
0	7.92×10^{11}
1	10.60×10^{11}
2	12.35×10^{11}
3	12.43×10^{11}

and its viscosity at 30° was at once determined by the torsion method. It was then maintained at this temperature for three days and viscosity determinations were made on each day. As can be seen from the results, the viscosity increased 34 percent in the first day, 22 percent in the second and only 1 percent in the third. Evidently as the semi-glassy glucose ages at this temperature, there is a rather marked annealing process taking place with a corresponding increase in the viscosity toward a certain equilibrium value.

TABLE IV. *Viscosities for various methods of preparation.*

Sample	η at 40°	η at 50°	η at 60°
A (vacuum)	3.6×10^{9}	4.2×10^{7}	—
B (")	3.0 "	3.6 "	1.06×10^{6}
C (in air)	2.6×10^{8}	5.5×10^{6}	2.8×10^{5}
D (")	1.3 "	3.2 "	1.9 "
"Best value" (Table I)	2.8×10^{9}	3.0×10^{7}	9.3 "

The mode of preparation of the liquid glucose has also an important influence on its viscosity. Ordinarily the samples were prepared by melting the crystals and heating this product under a vacuum for about five minutes at 155°. However, in order to ascertain the effects of a marked variation from these conditions, we first prepared four samples in this way and then subjected two of these (*A* and *B*) to an additional heating period of twenty-five minutes at 155° under a vacuum and the other two (*C* and *D*) to a similar heating in the open air. The viscosities of all four samples were then determined over a range of temperatures by the concentric cylinder method. In Table IV we have recorded the values at 40°, 50° and 60°, as these results are quite typical. From such data it is evident that the additional heating of the glucose under vacuum raises the viscosity to some extent, while the heating in open air produces a very marked lowering. In both cases the glucose sample became deep brown in color and some decomposition undoubtedly had taken place. However, with the vacuum any water thus formed was immediately removed; while the heating in air permitted accumulation of water in the sample with a consequent lowering in the viscosities.

THE VARIATION OF VISCOSITY WITH TEMPERATURE

The variation of liquid viscosity, or of its reciprocal—fluidity ($\phi=1/\eta$)—, with temperature has been considered previously by de Guzman, Drucker, Dunn, Andrade and Sheppard.[8] All these investigators obtain an equation

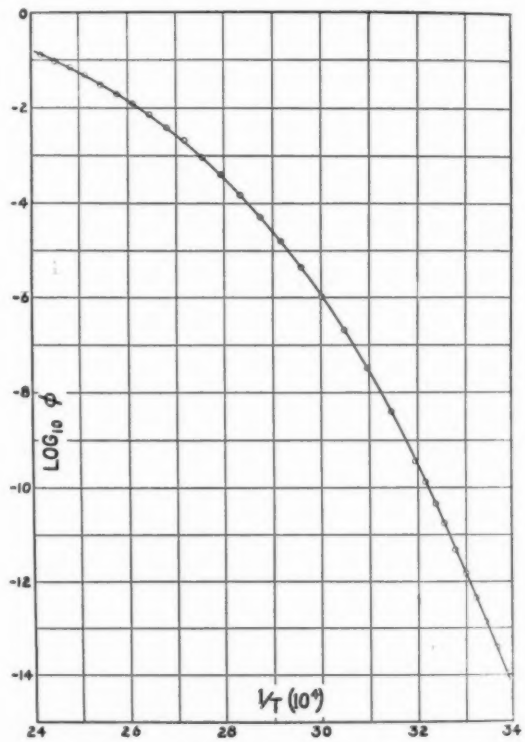

FIG. 3. The logarithm of the fluidity (ϕ) of undercooled liquid glucose plotted against the reciprocal of the absolute temperature.

[8] J. de Guzman, Anales soc. esp. fis. y quim. **11**, 353 (1913); C. Drucker, Zeits. f. physik. Chemie **92**, 287, 312 (1918); J. S. Dunn, Trans. Faraday Soc. **22**, 401 (1926); E. N. C. Andrade, Nature **125**, 582 (1930); and S. E. Sheppard, Nature 489 (1930).

which can be put into the form

$$d \log_{10} \phi/d(1/T) = -\Delta H/2.30R, \qquad (4)$$

where T is the absolute temperature, R is the gas constant for one mol, and ΔH is an energy quantity corresponding to the "heat of disorientation." Thus ΔH may be considered as a measure of the strength of the intermolecular fields within the liquid. In many cases it is of the same order of magnitude as the heat of fusion.

For "normal" liquids Sheppard and Houck[9] have shown that a plot of log ϕ against $1/T$ gives a practically straight line. That is, the value of ΔH is fairly constant. On the other hand, for associated liquids, such as water and formic acid, the curve departs from a rectilinear relationship in such a way as to give larger values for ΔH as the temperature is lowered and the degree of association presumably increases.

[9] S. E. Sheppard and R. C. Houck, J. Rheology **1**, 349 (1930).

Our undercooled liquid glucose represents a very extreme case of this associated type. In Fig. 3 we have plotted the logarithms of the reciprocals of the viscosity values given in Table I and from the slope of the resulting curve we find 20,000 cal., 30,000 cal., and 110,000 cal. for the values of ΔH at, respectively, 140°, 112° and 26°C. However, the heat of fusion of α-glucose per formula weight (180 grams) is only 7800 cal. at 146°, according to an unpublished investigation carried out in this laboratory; and an estimate, by Kirchhoff's law, for the hypothetical fusion process at 20° gives about 3700 cal. If therefore we are to obtain molal fusion values at all comparable to these large "heats of disorientation" found from the variation of viscosity with temperature, we must now postulate a very considerable and variable amount of association within this undercooled liquid glucose —perhaps, an association of the order of twenty to thirty formula molecules at 26°.

Viscosity Anomalies

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Translated from the French by E. C. Bingham
(Received March 28, 1934)

THE theory of Poiseuille accounts with satisfactory exactitude for the flow of pure liquids or of true solutions through capillary tubes.

The efflux Q is represented as a function of the gradient of pressure p per unit of length of the capillary tube and of the radius R, by the relation

$$A=(\pi R^4/8\eta)p, \tag{1}$$

η being the viscosity, independent of the time but a function of the temperature and the concentration of the solution.

For certain colloidal solutions the law of Poiseuille stating the proportionality between the efflux and the pressure is not verified at low pressures. These solutions present *viscosity anomalies*. The flow of these quasi-solutions through capillaries, according to Wo. Ostwald,[1] belongs in a special regime called the *structural regime*. Wo. Ostwald adopts the relation of deWaele,[2] F. D. Farrow and C. M. Lowe[3]

$$Q=Kp^n \qquad n>1 \tag{2}$$

analogous to that of the turbulent regime:

$$Q=Kp^{1/n} \qquad n=1.76 \text{ (Osborne)}. \tag{3}$$

This empirical formula scarcely enables one to answer the question as to whether there exists in these solutions a coefficient of viscosity conformable to the hypothesis of Newton-Navier. Let us restate that hypothesis. Between two layers of liquid moving at different velocities, on an element of the surface of separation dS there is a force in a direction opposite to the displacement of the element considered acting in a plane tangent to the surface and of an intensity proportional to the rate of variation $\partial v/\partial n$ of the velocity along the normal to the interface

$$dF=-\eta(\partial v/\partial n)dS. \tag{4}$$

The coefficient of viscosity η is independent of the velocity gradient.

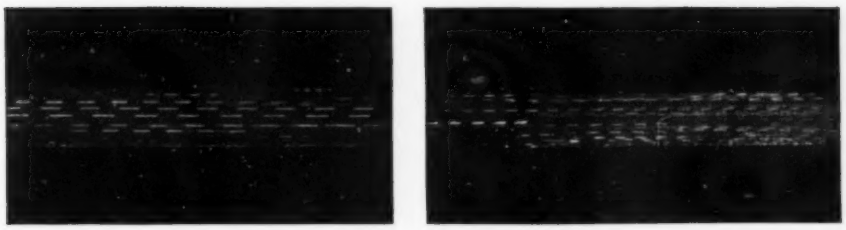
The Distribution of Velocities of Colloidal Solutions Presenting Viscosity Anomalies

In advance of any theory it is necessary to take into account the distribution of velocities in solutions presenting viscosity anomalies. We have made use of Professor Camichel's chronophotographic method. The method depends upon photographing small particles of aluminum in suspension in the fluid which are illuminated by appropriate means. The particles of aluminum appear as bright points on a dark ground. The particles of aluminum follow the movements of the liquid with the greatest fidelity. By making the lighting intermittent, when making photographs, the liquid threads are formed of discontinuous strokes; assuming a given period one may obtain a measure of the velocity by the simple measurement of a length upon the plate.

We have studied the distribution of velocities of liquids flowing under constant head between two parallel infinite planes. Fig. 1 represents the pattern of flow for pure water and for a 0.7 percent solution of gelatine three days after its preparation. Fig. 2 shows the distribution of velocities.

In the case of the gelatine solution, one cannot doubt the existence of a portion of the liquid which flows as a plug. For colloidal solutions, these experiments eliminate the empirical formulas of efflux or the theories of a distribution of velocities decreasing progressively from the axis of the capillary tube to the wall.

[1] Ostwald, Kolloid Zeits. **36**, 99 (1925).
[2] deWaele, J. Oil and Colour Chem. Assoc. **4**, 33 (1923).
[3] F. D. Farrow and C. M. Lowe, J. Textile Inst. **14**, 414 (1923).



Water Gelatine

FIG. 1. The flowing of water and a solution of gelatine between two parallel plates.

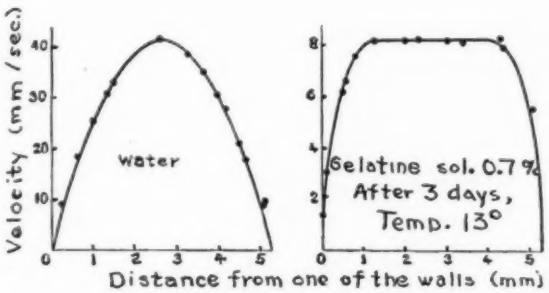


FIG. 2.

HYPOTHESIS OF STRUCTURAL FRICTION. DISTRIBUTION OF VELOCITIES AND EFFLUX

At a given temperature, with a given concentration, at a well-defined time in its history, we assume the following hypotheses for a colloidal solution, which is a liquid without true shape and not a gel.

1. The liquid flows in a capillary tube as coaxial cylinders moving with a velocity v as a function of the radius r;

2. On the surface of each cylinder there are impressed:—(a) Tangential forces of viscosity, according to the hypothesis of Newton-Navier. These forces are expressed for an element of surface dS

$$dF_1 = \eta(dv/dr)dS, \tag{5}$$

where dv/dr is the rate of variation of the velocity normal to the interface. (b) Tangential forces due to the friction of the colloidal particles on each other opposite in direction to the displacement of the element under consideration, proportional to the surface and independent of the pressure

$$dF_2 = a\,dS \tag{6}$$

where a is by definition the coefficient of *structural friction.*

3. The velocity of the liquid is zero at the wall. For a cylinder of radius r and of length equal to the unit of length, there is a force acting down-stream, $p\pi r^2$, where p is the difference of pressure at the ends of the cylinder, and tangential forces up-stream

$$-\eta dv/dr \cdot 2\pi r + a \cdot 2\pi r. \tag{7}$$

For a steady state

$$\begin{aligned} p\pi r^2 &= -\eta dv/dr \cdot 2\pi r + a \cdot 2\pi r, \\ pr &= -2\eta dv/dr + 2a, \end{aligned} \tag{8}$$

whence

$$-dv/dr = (1/\eta)(pr/2 - a). \tag{8_2}$$

This is the mathematical expression of the theory of Buckingham[4] and of Bingham.[5] Let us assume that

$$2a = pr_0, \tag{9}$$

$$-\eta dv/dr = (p/2)(r - r_0). \tag{10}$$

As dv/dr is negative, one has the condition, $p > r_0$. The elements situated within the cylinder of radius r_0 all have the same velocity v_0. Let us calculate the velocity v of the cylinder of radius r, making use of the third hypothesis. On integration one obtains

$$2\eta v = (p/2)[(R - r_0)^2 - (r - r_0)^2]. \tag{11}$$

The velocity v_0 of the elements within the cylinder of radius r_0 becomes

$$2\eta v_0 = (p/2)(R - r_0)^2. \tag{12}$$

Under the head p, the distribution of velocities of the elements forming the liquid is as follows: the velocity is uniform on the interior of the

[4] Buckingham, Proc. Am. Soc. Testing Mats. **21**, 1154 (1921).

[5] Bingham, Bull. U. S. Bur. Stand. **13**, 309–352 (1916). *Fluidity and Plasticity*, McGraw-Hill Book Co., New York, pp. 222–226 (1922).

cylinder of the radius r_0, the distribution is parabolic from this cylinder to the wall of the tube.

If we consider the flow of this liquid between two parallel unlimited planes, the distribution of velocities is analogous. The velocity of the different elements of the liquid is the same between two planes parallel to the median plane situated at a distance r_0 from it, the distribution of the velocities being parabolic from this plane to the walls.

This theoretical distribution of velocities is confirmed by the study of the hydrodynamic pattern of velocities of 0.7 percent of gelatine solution, three days old at a temperature of 13° flowing between two parallel planes which can be assumed to be infinite (Fig. 1).

The Pressure Limit

The velocities of the different elements approach zero as r_0 approaches R. The liquid contained in the capillary tube under the action of a difference of pressure p_1 per unit length does not flow any more. This pressure p_1 is the pressure limit,

$$p_l R = 2a. \tag{13}$$

Evaluating the efflux

$$Q = \pi r_0^2 v_0 + \int_{r_0}^{R} 2\pi r v dv,$$

and on integration,

$$Q = \frac{p\pi R^4}{8\eta}\left[1 - \frac{4}{3}\frac{r_0}{R} + \frac{1}{3}\left(\frac{r_0}{R}\right)^4\right]. \tag{14}$$

For an ordinary viscous liquid,

$$r_0 = 0, \quad Q = p\pi R^4/8\eta.$$

Flow of a Liquid Under the Influence of Pressure

The cylindrical pressure tube (Fig. 3) is connected to a bath at constant level by a horizontal capillary tube. The difference of pressure at the ends of the capillary tube is due to the vertical difference in the levels of the free surfaces in the pressure tube and in the bath at constant level. Denoting this difference in level by h, the length of the capillary tube by L, the acceleration of gravity by g, and the specific gravity of the liquid by ρ, we obtain $Lp = h\rho g$.

The yield value of p_l is found to be connected with the limiting difference in level h_l by the relation

$$Lp_l = h_l \rho g. \tag{15}$$

We have in addition from (9) and (13)

$$pr_0 = 2a = p_l R,$$

whence

$$r_0/R = p_l/p = h_l/h, \tag{16}$$

from which we obtain the new expression for the efflux in terms of measurable quantities,

$$Q = \frac{\pi R^4}{8\eta} \cdot \frac{\rho g h}{L}\left[1 - \frac{4}{3}\frac{h_l}{h} + \frac{1}{3}\left(\frac{h_l}{h}\right)^4\right], \tag{17}$$

where η and h_l are constants of the apparatus and of the liquid.

Experiments

We do not measure the efflux but the time t required by the level of liquid in the pressure-tube to pass from the level h_0 to the level h.

Denoting by S the constant section of the pressure tube,

$$Qdt = -Sdh, \tag{18}$$

$$\frac{\pi R^4}{8\eta}\frac{\rho g}{Ls}t = \int_h^{h_0} \frac{dh}{h\left[1 - \frac{4}{3}\frac{h_l}{h} + \frac{1}{3}\left(\frac{h_l}{h}\right)^4\right]}, \tag{19}$$

Change of Variable

Let us take the quantity x as an auxiliary variable, defined by the relation

$$h/\tfrac{1}{3}h_l - 4 = x, \tag{20}$$

where x is a number.

We will assume that

$$\tfrac{1}{3}h_l = \alpha, \tag{21}$$

so that

$$2a = p_l R = (h_l/L)\rho g R,$$

whence

$$\alpha = 2(a/3)(L/R)(1/\rho g), \tag{21$_2$}$$

where α is a constant of the capillary tube and of the liquid of given concentration temperature and at a specified stage of its history.

We will assume in addition that

$$(M\pi R^4/8\eta)(\rho g/Ls)=A, \qquad (22)$$

where $M=1/2.303$ is the logarithmic modulus, A is a constant of the apparatus at the given concentration, temperature and at a specified stage of its history. For a particular apparatus, α is proportional to the coefficient of structure a and A is inversely proportional to the coefficient of viscosity. The differential Eq. (18) becomes

$$2.303\,A\,dt=-\frac{(x+4)^3}{(x+1)^2(x^2+10x+27)}dx.$$

We get,

$$\int\frac{(x+4)^3dx}{(x+1)^2(x^2+10x+27)}=\frac{3}{2}\frac{1}{x+1}-\frac{5}{6}\log(x+1)-\frac{1}{12}\log(x^2+10x+27)-\frac{\sqrt{2}}{12}\arctan\frac{x+5}{\sqrt{2}}+\cdots.$$

Assuming

$$\Phi(x)=\frac{5}{6}\log(x+1)+\frac{1}{12}\log(x^2+10x+27)+\frac{\sqrt{2}}{12\cdot 2.303}\arctan\frac{x+5}{\sqrt{2}}-\frac{3}{2\cdot 2.303}\frac{1}{x+1}. \qquad (23)$$

the Eq. (19) becomes:

$$At=\Phi(x_0)-\Phi(x). \qquad (24)$$

Description of the Apparatus

Fig. 3 is a diagram of the apparatus. The liquid flows out through the capillary tube from the pressure tube into the bath of constant level. The pressure tube is approximately cylindrical and is easily measured. The joint between the pressure tube and the vertical branch of the tube A is made tight, by grinding with emery. The ends of the horizontal branch of the tube A are closed by rubber stoppers, the one holding the capillary tube and the other one a branch of the three-way stopcock R.

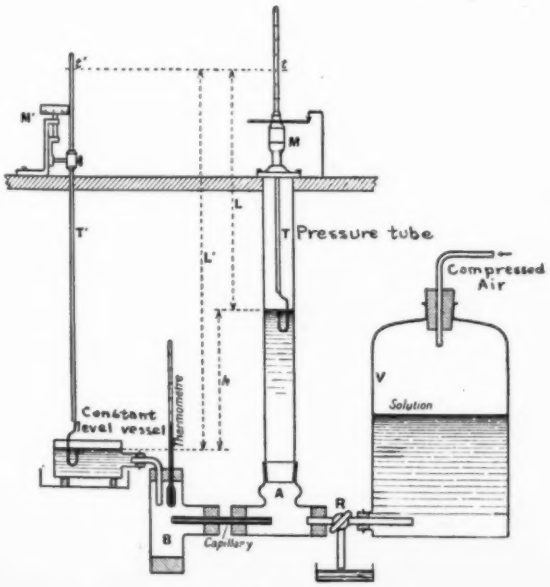


Fig. 3.

The capillary empties into the tube B through a rubber stopper. The vertical branch of this tube is closed at its lower end by a solid stopper, at its upper end by a stopper carrying a 1/10° thermometer and by a tube connected on the other side with the constant level bath. This bath was made specially for this purpose. One of the faces formed a weir, and the liquid which overflows is caught in a dish.

In an experiment the solution is introduced into the vessel V. This is connected to the pressure tube by means of the three-way stopcock R. Air pressure is applied above the liquid in vessel V. Turning the cock R allows putting on the pressure without froth or bubbles on the surface of the liquid or the partial or complete removal of the liquid. The entire apparatus was placed in a thermostat, the temperature being held constant to nearly 0.2° for several days. The thermostat is closed by a double door. The interior door is set with solid plate glass; the second is of window glass over the greater part of its surface. To open or close the cock R it is necessary to open the two doors, but in working quickly, this does not result in any disturbance

of the temperature of the liquid. Some small shutters were made in the middle of the door which permitted the observer to make various observations without having to open up the interior of the thermostat.

Measure of the Variation of Level of the Liquid in the Pressure Tube and of the Time

We need to measure: (1) The height of the free surface, of the liquid in the pressure tube above the free surface of the bath when full. (2) The time t used by the liquid in passing from a pressure h_0 to a pressure h. The free surface of the liquid in the pressure tube is read by the aid of an index carried by the rod T. Some very fine divisions about 2 cm apart are traced on this rod. The index which it carries is a phonograph needle. The distances L, from the extremity of the index to the different divisions of the rod, are measured very exactly on a comparator. The rod can be displaced by considerable friction in the direction of the screw micrometer M. The mandrel or chuck of this screw allows more or less of adjustment of the rod to the screw. The rotation of the screw micrometer displaces vertically the extremity of the index by exactly measured amounts. The pitch of the screw is 0.5 mm, the head has a diameter of 16 cm.

The free surface in the completely filled vessel is read by means of the index carried by the rod T'. At the other end of the rod, there is traced a fine line t'. The distance L' between this mark and the end of the index is measured with a comparator. The rod T' is held by a micrometer screw M' and the index is brought into contact with the free surface of the liquid in the full tube. While viewing with a cathetometer by sliding T into the mandrel of the screw M a mark t of the rod T is brought into the horizontal plane passing through the mark t' on the rod T'. The distance between the two indices is $h=L'-L$.

The free surface of the liquid within the pressure tube is illuminated from the side by means of a small 4-volt electric lamp. The surface of the liquid above the index is uniformly illuminated for the observer receiving the light. A little dark meniscus appears bright where the point of the needle point is cut by the free surface of the liquid. The head at this moment is h_0.

At the moment that the meniscus appears the observer starts a stopwatch. The rod T is then lowered exactly 1 cm by turning the micrometer screw M exactly 20 turns.

One stops the watch when the index of the needle again pierces the free surface of the liquid. At this instant, the pressure is:

$$h=h_0-1 \text{ cm.} \tag{24_2}$$

Determination of A and of α

For a given colloidal solution, we have supposed that there exists a coefficient of viscosity and a coefficient of structure. A and α are independent of the pressure.

$$A=M(\pi R^4/8)(\rho g/Ls), \tag{22}$$

$$\alpha=(2a/3)\cdot(L/R)\cdot(1/\rho g). \tag{21_2}$$

On the other hand, the determination of A and of α make it possible to calculate η and a. For an initial head h_0 experiment supplies the time t corresponding to the passage of fluid at the head

$$h=h_0-1. \tag{24_2}$$

If we assume that

$$x_0=h_0/\alpha-4, \tag{25}$$

$$x=h/\alpha-4, \tag{26}$$

$$\Phi(x)=\frac{5}{6}\log(x+1)+\frac{1}{12}\log(x^2+10x+27)$$

$$+\frac{\sqrt{2}}{12\cdot 2.303}\arctan\frac{x+5}{\sqrt{2}}-\frac{3}{2\cdot 2.303}\frac{1}{x+1}, \tag{23}$$

we obtain

$$At=\Phi(x_0)-\Phi(x). \tag{24}$$

For a given h_0, A is then a function of α given by the use of the relations (24_2), (25), (26) and (23), we can construct the curve corresponding to $A=f(\alpha)$. For $\alpha=0$ (the law of Poiseuille) Eq. (24) becomes

$$At=\log(h_0/h)=\log(h_0/h_0-1)$$

and the tangent to the curve $A=\phi(\alpha, h_0)$ has for angular coefficient

$$\left(\frac{dA}{da}\right)_{a=0}=\frac{1}{t}\frac{4}{2.303}\left[\frac{1}{h}-\frac{1}{h_0}\right]=\frac{1}{t}\frac{4}{2.303\cdot h_0}(h_0-1).$$

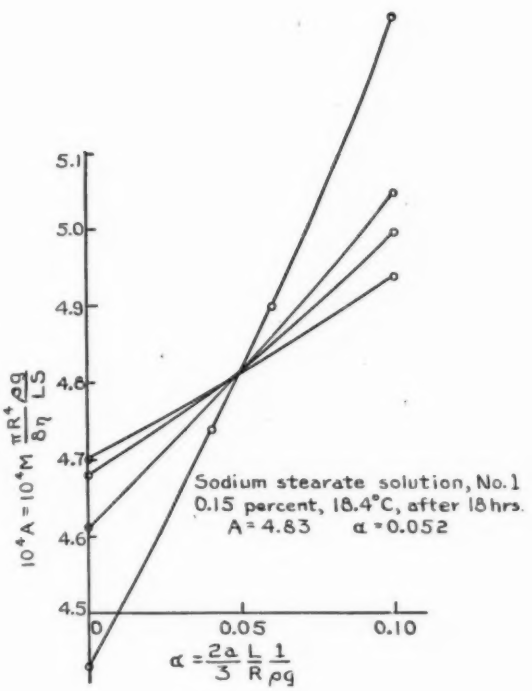


FIG. 4.

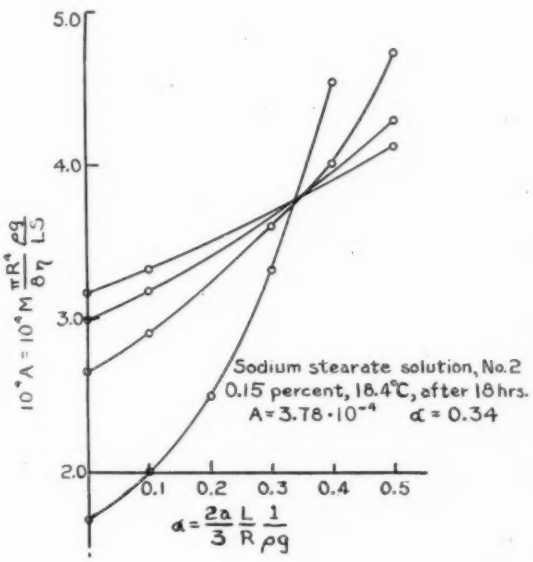


FIG. 5.

If our hypotheses are correct, the curves corresponding to the different values of h_0 pass through the same point; the coordinates of this point A_0 and α_0 are the values of A and α for the liquid under consideration. In reality the different curves h_0 = etc. pass very sensibly through the same point in practice as the graphs show in Figs. 4, 5 and 6 for different solutions of sodium stearate.

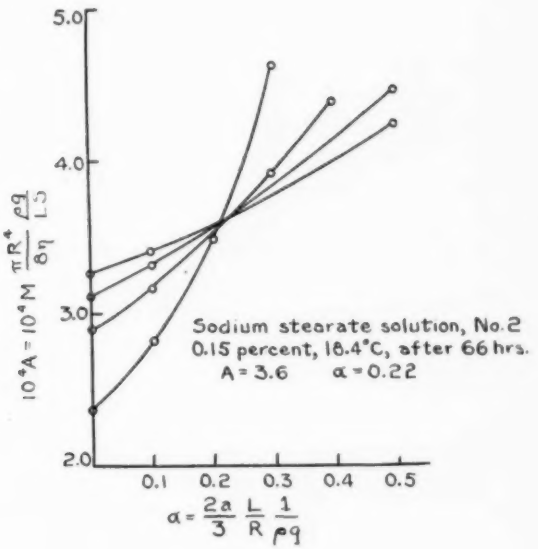


FIG. 6.

SODIUM STEARATE SOLUTIONS

The solutions of sodium stearate present the anomalies in viscosity so often reported by Wo. Ostwald, his collaborators and numerous scientists for many colloidal solutions. In an earlier work[6] we have already studied the anomalies in viscosity of solutions of gelatine. The present paper has to do with the anomalies of viscosity of soap solutions and in particular of solutions of sodium stearate.

For a given concentration of sodium stearate there exists a temperature above which the coefficient of structure is practically zero; the liquid behaves like an ordinary liquid without viscosity anomalies. Below this temperature anomalies of viscosity appear. At a given moment in the history of a solution we determine a coefficient of viscosity and a coefficient of structure.

For a given temperature and concentration of sodium stearate, the coefficients depend upon the history of the solution. Sodium stearate appears to be particularly typical from this point of view. We have prepared two solutions of sodium stearate with 1.5 g per liter of two different makes.

[6] M. Pichot, J. de Physique [7] 3, 205–218 (1932).

First Solution

We dissolved 1.5 g of sodium stearate in a liter of water at 80°. We filtered the liquid at this temperature through a plug of cotton, then we placed it in a thermostat, where it finally took the constant temperature of 18.4° for the remainder of the experiment. Eighteen hours after the preparation of the solution, we made, in the same thermostat, the measurements for the determination of both the coefficient of structure and the coefficient of viscosity. The results are given in Table I.

Table I. *Solution 1. After 18 hours at 18.4°C temperature.*

h_0 (cm)	h (cm)	t (sec.)	$10^4 A$ for $\alpha=0.00$	$\alpha=0.03$	$\alpha=0.05$	$\alpha=0.10$	$10^4(dA/d\alpha)_{\alpha=0}$
9.085	8.085	107.6	4.70			4.94	2.20
7.085	6.085	141.2	4.68			4.99	2.85
5.075	4.075	206.8	4.61			5.05	4.07
3.065	2.065	386.8	4.43	4.74	4.90	5.28	7.09

Fig. 4 represents the curves corresponding to $A=f(\alpha)$. They furnish for the values of A and of α:—$A=4.83\cdot10^{-4}$, $\alpha=0.052$. We have $R=0.041$ cm, $L=15.1$ cm, $S=4.987$ cm², $\eta=1.24$ centipoise, $a=0.41$ barye.

Second Solution

We dissolved 1.5 g of sodium stearate in 500 cm³ of water at 80°. After filtering hot, the liquid was slowly cooled. From 40° one obtains a gel. Completing the solution to a liter, the solution was reheated to 80°. The liquid was then placed in the thermostat and the experiments carried out 18 hours after the preparation of the solution. The results are given in Table II. Fig. 5 represents the curves corresponding to $A=f(\alpha)$. They furnish for the values of A and of α:—$A=3.78$ and $\alpha=0.34$, hence $\eta=1.58$ centipoise, $a=2.72$ baryes. With this second solution, we measured the coefficient of viscosity and the coefficient of structure 66 hours after preparation. The results of the experiments are given in Table III. Fig. 6 represents the curves corresponding to $A=f(\alpha)$. They furnish for the values of A and of α:—$A=3.6\times10^{-4}$, $a=0.22$, whence $\eta=1.66$ cp, $a=1.76$ baryes.

Table II. *Solution 2. After 18 hours at 18.4°C temperature.*

h_0 (cm)	h (cm)	t (sec.)	$10^4 A$ for $\alpha=0.00$	$\alpha=0.10$	$\alpha=0.30$	$\alpha=0.40$	$\alpha=0.50$
9.085	8.085	159.8	3.17	3.32			4.14
7.085	6.085	222.8	2.99	3.19			4.30
5.075	4.075	358.1	2.66	2.92	3.61	4.03	4.74
3.065	2.065	1011.4	1.69	2.02	3.32	4.55	7.55

Table III. *Solution 2. After 66 hours at 18.4°C temperature.*

h_0 (cm)	h (cm)	t (sec.)	$10^4 A$ for $\alpha=0.00$	$\alpha=0.10$	$\alpha=0.20$	$\alpha=0.30$	$\alpha=0.40$	$\alpha=0.50$
9.085	8.085	155.6	3.25	3.41				4.25
7.085	6.085	212.	3.12	3.32				4.48
5.075	4.075	329.	2.90	3.17		3.93	4.39	5.15
3.065	2.065	722.2	2.37	2.83	3.49	4.64	6.38	

In conclusion, the coefficient of viscosity of the second solution varied but little between the 18th and the 66th hour. The coefficient of structure decreased. But these coefficients are considerably different from those of the first solution. The history of the solution is brought out here very clearly.

Some Rheologic Aspects of Petroleum Production

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A critical review and summary are given of some of the rheological aspects of the production and transportation of petroleum. It is shown how the proper flow characteristics of the colloidal dispersions known as drilling fluids may be controlled by chemico-physical methods, and the importance of these characteristics in the technique of drilling is analyzed. The laws of flow of gas-oil mixtures through porous media are approached by a study of the permeability factor of such media, and applied to the problems of ultimate production, production rate, effective drainage area, etc., of petroleum-producing horizons. The flow of gas-liquid mixtures through pipes is discussed from the standpoint of bringing oil to the surface from the reservoir. Pipeline flow of oil is discussed with particular reference to cold weather flow for oils that exhibit thixotropic properties because of a heavy content of wax. Unsolved problems in these various fields of the rheology of petroleum production are pointed out.

I. Introduction

THE science of rheology assumes an important rôle in the production and transportation of petroleum from the initial stage of drilling the well to the delivery of the crude to the refinery through pipe lines. In the rotary method of sinking the bore hole, circulation of a colloidal suspension of clay or inert material, such as barite, is a necessary part of the operation. It is only recently that petroleum technologists have had a full appreciation of the importance of adequate control by chemico-physical methods of rotary drilling fluid, including a study of the flow characteristics of such colloidal suspensions. Modern developments in the technique of drilling with these colloidal suspensions have been directed toward lowering the viscosity and, at the same time, maximizing their thixotropic properties. When the producing horizons are penetrated it is essential to have a knowledge of the flow of gas and petroleum through porous media in order to govern the production rate most efficiently and to predict the ultimate production, effective drainage area, pressure decline, etc., of the well. The flow of mixtures of gas and oil through the string of flow tubing involves the unsolved problem of two-phase flow. The transportation of petroleum through pipelines is governed by the well-known laws of flow through open conduits, but the problem is complicated by the thixotropic nature of petroleum heavy in wax when winter temperatures are encountered. In this paper we shall endeavor to give a critical review of the more recent developments in these various phases of the rheology of petroleum production.

II. Flow of Homogeneous Fluids Through Porous Media

In order to understand the ultimate production, production rate, effective drainage area, pressure decline, well spacing and methods of repressuring, it is essential that we have accurate knowledge of the flow of simple fluids and gas-liquid mixtures through porous media, such as reservoir rocks and sands, both consolidated and unconsolidated. Perhaps the most important specification of an actual oil reservoir is its permeability, as a measure of its capacity to flow gas or oil, for a fluid of given characteristics and under a known pressure gradient. With this object in mind several papers have recently appeared giving methods of measuring permeability for porous media for homogeneous fluids, and have discussed the application of such measurements to field conditions. Laboratory measurements have been confined chiefly to the study of the laws of flow of homogeneous fluids through porous media, while similar laws for gas-liquid mixtures are not yet known.

Two distinct methods of approach to the problem have been made: (1) an endeavor to correlate flow through porous media with the hydraulics of fluid flow through circular and

open pipe by obtaining a friction chart, where the friction factor f as calculated from Fanning's equation is plotted as a function of the Reynolds number on a logarithmic chart; (2) direct measurement of permeability, either in the laboratory or from field data on producing wells.

1. Laboratory measurements

Several methods have been used to evaluate the coordinates in the friction chart; for example, Chilton and Colburn[1] evaluate the velocity in the equations as v/F, where v is the velocity based on gross cross-sectional area and F is the fractional effective free area, while the diameter term refers to the average diameter of the conduits, or interstices between the particles, and as an approximation they are assumed to be equal to the average particle diameter. Chalmers, Taliaferro and Rawlins[2] define the diameter term as the mean effective pore diameter, a hypothetical quantity equivalent to the diameter of a capillary tube which will flow the same amount of fluid under the same pressure conditions as will flow through the tortuous path of a single series of interconnected pores. In the region of viscous flow this term may be calculated when proper data from flow measurements are introduced into Poiseuille's equation. Wilde and Moore[3] also use the conception of effective pore diameter in their paper on the hydrodynamics of reservoir drainage. It should be borne in mind, however, that the mean effective pore diameter as measured in this manner, without taking into account several important corrections, is not the true value of the hypothetical quantity. Bartell and Osterhoft[4] have analyzed such measurements in detail and have shown that the diameter as measured from flow data must be corrected by the factor $\pi/2$ to check with the diameter as measured by the capillary-rise method. It seems more logical, therefore, to evaluate the effective area factor by a measurement that more nearly corresponds to the actual cross-sectional area of the media under examination in the flow experiment. Fancher and Lewis[5] have calculated the friction factor by inserting the average grain diameter d in Fanning's equation, where d is calculated from a screen analysis of the material broken down, in the case of consolidated sands, as nearly as possible to grain size. The latter authors found that the data for three unconsolidated sands of different porosities correlated and aligned fairly well on a friction chart, by using air, water and crude oil as the flowing fluids over a series of pressure drops. Similar data for consolidated sands, however, did not align on a single curve, but gave a series of parallel curves displaced from that for unconsolidated sands by amounts depending on the value of the grain diameter, the amount and distribution of cementing material, and the degree of angularity of the grains. The curve obtained on the friction chart showed a fairly definite zone in which the flow changed from viscous to turbulent, as in the case of fluids in pipes, while Chalmers *et al.*[3] obtained a continuous curve without an abrupt break in its continuity.

Permeability may be calculated from the friction chart by a combination of Darcy's law and Fanning's equation. Using the friction chart of Fancher and Lewis (reference 5), the permeability of a sand for a given fluid may be computed from the screen analysis of the sand and the properties of the fluid at the temperature of flow by assuming desired dimensions and a rate of flow, from the equation $K = gd^2/2C\eta$, where K is the permeability, d is the diameter of the average grain, C is a constant characteristic of the sand, and η is the absolute viscosity at the temperature of flow. For precision in the case of consolidated sands it is necessary to classify the sand under examination, in addition to the screen analysis, with respect to porosity, distribution of sizes of grains, appearance of the sand under the microscope, and its geologic history and relationships. The alternative is to determine one point by experiment in the viscous region in addition to the screen analysis, taking advantage of the fact that the slope of each line on the friction chart is -1.

In the case of production from underground reservoirs the flow is viscous in practically all cases, except within a very short distance of the well bores producing at high rates. For this reason we shall be interested primarily only in

[1] Chilton and Colburn, Ind. Eng. Chem. **23**, 913 (1931).
[2] Chalmers, Taliaferro and Rawlins, Trans. Am. Inst. Mining and Met. Engrs. Pet. Div. **98**, 375 (1932).
[3] Wilde and Moore, Oil Weekly **67**, No. 12, 34 (1932).
[4] Bartell and Osterhoft, J. Phys. Chem. **32**, 1553 (1928).
[5] Fancher and Lewis, Ind. Eng. Chem. **25**, 1139 (1933).

the region of viscous flow, as applied to oil and gas wells. It is most satisfactory, as suggested by Wyckoff, Botset, Muskat and Reed[6] to define the permeability of a sand as the macroscopic velocity of a particle of a unit viscosity fluid at a point in the medium at which the pressure gradient is unity, so that in the viscous region of flow the permeability of the porous medium is independent of the absolute pressure or velocities within the flow system, or of the nature of the fluid, and is characteristic only of the structure of the medium. As these authors point out, the permeability constant is a macroscopic dynamical characterization of the nature of the sand, and should be determined dynamically by an actual flow experiment. It is illogical to attempt to correlate permeabilities with a single non-dynamical property of the sand, such as porosity, grain size distribution as obtained from sieve analysis, etc., for the permeability is a function of several variables, such as degree of cementation, angularity of grains, and degree of uniformity of grain size distribution, which may vary although the grain-size distribution remains essentially constant. It is preferable to make a permeability measurement for any given sample, using air as the flowing fluid. Such a measurement is made very quickly once the apparatus is assembled, and the use of gas eliminates the difficulties experienced with liquids.[7]

The permeability K for viscous flow is defined by the transposed form of Darcy's law

$$K=\eta v/(dp/dx),$$

where η is the viscosity of the flowing fluid, v is the velocity along the x-axis of the flow channel in a column of uniform section of the sand, and dp/dx is the pressure gradient. For liquids v is constant, hence the pressure gradient is constant; then

$$K=\eta QL/A(P_1-P_2),$$

where Q is the volume of liquid passing through an area A of the flow channel of length L in unit time, and P_1-P_2 is the pressure drop measured at the terminals of the sand sample. If gas is the flowing fluid, the mass velocity, or dp^2/dx is a constant, equal to $(P_1^2-P_2^2)/L$; then

$$K=2\eta QpL/A(P_1^2-P_2^2)=\eta\overline{Q}L/A(P_1-P_2),$$

where Q is the volume of gas at pressure p flowing through the sand sample in unit time, and $\overline{Q}$ is the volume at the mean pressure. The data obtained are plotted with Q/A or $\overline{Q}/A$ as a function of (P_1-P_2), giving straight lines of slope K/η passing through the origin for viscous flow and curves bending toward the axis of abscissae for turbulent or partially turbulent flow.

It is to be noted that most investigators agree as to the technique for permeability measurements and even as to its definition in the case of viscous flow. However, there is a difference of opinion as to the significance of the friction factor charts. While admitting that such charts make possible the extrapolation of the permeability to high Reynolds numbers, the fact that in field problems of practical interest the flow conditions will almost always be viscous except possibly for the few inches immediately adjacent to the sand face, leaves only an academic interest in such extrapolations. Furthermore, when the flow conditions are turbulent it is questionable if the definition of the permeability by the ratio $QL/A\Delta p$ is any longer valid, as this ratio will vary with the velocity of flow.

On the other hand, the question may be raised as to the reliability of using the charts for consolidated sands. For in view of the wide variation among the various curves for consolidated sands—the "constant" C of Fancher and Lewis varies by a factor of 175—the sieve analysis alone will not suffice to determine the curve on the friction factor chart. And even if a permeability measurement be made to locate the curve it would appear quite probable that another sample even from the same sand, which for some reason has a different permeability, will for the same reason belong to another curve. It would, therefore, seem that a direct permeability measurement would ultimately be necessary in addition to the sieve analysis for almost each sand sample and as the ultimate purpose is to find the permeability, it is questionable if the sieve analysis would add a great deal of practical information. In fact, it would seem that the work of Fancher and Lewis shows rather the difficulty and impracticability of accurately cor-

[6] Wyckoff, Botset, Muskat and Reed, Physics **4**, 394 (1933).

[7] Muskat and Botset, Physics **1**, 27 (1931).

relating the permeability of consolidated sands with porosity or grain size, than the usefulness of sieve analyses in replacing direct permeability measurements, which incidentally can be made in a very few minutes once the apparatus has been assembled.

2. Field measurement of permeability

Although the technique for measuring the permeability of sand cores in the laboratory has been well standardized, it is desirable to measure the permeability of the producing sand *in situ*, for fractures or voids in the formations may result in an effective permeability far different from the laboratory measurement on a single core. Wyckoff, Muskat and Reed,[6] Muskat and Botset[7] and Moore, Schilthuis and Hurst[8] have shown how such measurements may be made in the field. Again starting with Darcy's law, V is now the radial velocity, and is given by $V=Q/2\pi rh$ where Q is the total volume rate of flow into the well and h is the sand thickness. Applying potential theory it follows for the flow of dead liquid that

$$K=(\eta Q \log r_e/r_w)/2\pi h(P_e-P_w),$$

where P_w is the bottom hole pressure, or pressure at the face of the well defined by the radius r_w of the borehole and P_e is the pressure at a large distance from the well, and which may be identified with the formation pressure. For a gas well, it follows that

$$K=(\eta \overline{Q} \log r_e/r_w)/2\pi rh(P_e-P_w).$$

In applying these equations, η may be determined in the laboratory, Q and $\overline{Q}$ by standard flow meters, P_w by a bottom hole pressure gauge, and r_w and h from the drilling record. P_e may be taken as the bottom hole pressure with the well shut in after sufficient time has elapsed for transients in the sands to dissipate themselves. It may also be determined graphically as the intercept on the P_w axis, in the case of liquids, if Q is plotted as a function of P_w, or, in the case of gas wells, as the intercept on the P_w^2 axis, if the rate of gas flow, reduced to standard conditions, is plotted as a function of P_w^2. The curves in each case are linear for the production of homogeneous fluids flowing in the viscous zone. There is no exact method of choosing r_e, but practically it may be taken as half the distance to the nearest neighboring well without appreciable error, for the variation of K is logarithmic. Corrections may also be applied in case the bore hole does not completely penetrate the producing horizon.

Wyckoff, Botset and Muskat[9] have also shown that in the case of wells flowing under artesian and gravity flow combined that

$$K=(\eta Q \log r_e/r_w)/\pi\rho g(2h_e h_e-h_e^2-h_w^2),$$

where ρ is the density of the liquid and $g=0.00097$ atms. per unit density, h_e is the total fluid head measured from the bottom of the sand after the pumps have been stopped for a sufficient period of time to permit the fluid level to reach its normal height in the well, h_e is the height of producing sand, and h_w is the fluid head in the pumping well, measured from the bottom of the sand.

It is to be noted that the above equations apply only for the flow of gas or dead liquids, since rigorous formulae for the flow of gas-liquid mixtures are not known owing to the lack of flow data for two-phase fluids through porous media. The equations apply with reasonable accuracy however to liquids with dissolved gas, for the viscosity term may be altered for these cases; also field tests may be made with high back pressures to minimize the volume of free gas within the media.

Moore, Schilthius and Hurst[8] have shown how the average permeability of the entire sand section around a well to fluids as they exist in the reservoir may be obtained from field measurements, basing their method on a mathematical analysis for the case of flow in the unsteady state, i.e., where pressures and velocities through the reservoir are continuously changing. The method is based on the solution of the differential equation

$$\frac{\partial \rho}{\partial r^2}+\frac{1}{r}\frac{\partial \rho}{\partial r}=\frac{c\varphi}{K}\frac{\partial \rho}{\partial \theta}$$

for the two cases (1) the pressure at the well is constant, (2) the rate of production is constant,

[8] Moore, Schilthuis and Hurst, Paper presented at the Tulsa meeting of A. P. I. May 18, 1933.

[9] Wyckoff, Botset and Muskat, Physics **3**, 90 (1932).

where ρ is the density of the oil-gas mixture, r is the radius of the reservoir, c the compressibility of the oil-gas mixture, K the permeability, φ the fractional porosity and θ the time. The interpretation of the solutions of the equations is simplified by a graphical representation, plotting certain ratios of the important variables. The field data required to calculate the permeability by the method of these authors are:

1. Thickness of producing sand drained by the well.
2. Diameter of the bore hole.
3. The compressibility of the oil-gas mixture.
4. Data from a flowing test on a well: (a) the variation in the pressure at the face of the producing sand with time during the test, (b) the variation in casing pressure, (c) the oil and gas production during the test.

It is important to note the difference in approach to the problem as given by Wyckoff, Botset and Muskat and by Moore, Schilthuis and Hurst. The former treat the problem of flow in a reservoir as a continuous succession of steady states, equivalent to the assumption that the velocity of the flow is negligible compared to the velocity of propagation of disturbances through the sand formation, while the latter treat the problem as flow in the unsteady state, one in which the pressures and velocities through the reservoir are continuously changing, and thereby solve the problem for the two special cases: (1) the pressure at the well remains constant, (2) the production rate remains constant. The equations of Moore, *et al.*, do not apply to gas-flow and reduce to dead liquids in the limiting case of vanishing compressibility. The equation of flow in the unsteady state, which contains the compressibility of the flowing liquid, will apply most advantageously to the long time transients in the case of production by water drive, where the compressibility of a large expanse of water will be of maximum importance.

Although the compressibility of the fluid will certainly have to be taken into account explicitly in any satisfactory theory of the flow of gas and oil into a well, it seems unlikely that the application of a theory of compressible homogeneous fluids to the rapid transients following a shut-down or opening of a well will give even approximately correct values of the permeability. For as long as there is free gas in the sand, the very elasticity of the gas-oil mixture will involve—because of the separation of the gas and liquid phases—rapid variations in the apparent permeability of the medium, which is not taken into account by the homogeneous compressible fluid theory. However, when the gas-liquid mixture flow has reached a steady state, the ordinary formulae, leaving out the compressibility of the mixture, should give quite accurate values of the effective permeability, as it is affected by the presence of the free gas for the particular stage in the whole history of the system which has been reached at the time of the measurement. As a field is depleted and free gas becomes disseminated throughout the media this effective permeability will change, but the rate of variation of the pressure and permeability conditions in a sand due to the natural depletion of its fluids is so slow as compared to the very rapid transients which are localized immediately about a well and are due to rapid changes in the well pressure—as in the case of shutdown or sudden opening—that they should be quite accurately represented as a continuous succession of steady states.

3. Flow of gas-liquid mixtures through porous media

Practically nothing is known about the general law of flow of gas-liquid mixtures through porous media, although considerable attention is now being devoted to these more complex systems. However, the experimental difficulties are so great and the number of variables involved are so large that it will probably be some time before the empirical results will permit a formulation that will be of practical value.

III. The Rheologic Properties of Rotary Drilling Fluids

The rotary method of drilling oil wells, as its name suggests, consists in rotating a column of pipe with a cutting tool, or bit, attached at the lower end. Powerful pumps circulate either water or a mud-laden fluid down this pipe and up the annular space between it and the walls of the hole.

The use of water causes caving in other than rock formations and, as will be made clear by the following, it does not have the necessary properties for ordinary drilling. The usual

drilling fluid is a suspension of clay in water but for special purposes substances of higher specific gravity are added.

The functions of a drilling fluid, in general, are to:

1. Plaster the walls of the hole, preventing caving.
2. Lubricate the cutting surface and cool the bit.
3. Carry cuttings from the bit to the surface and deposit them.
4. Furnish sufficient hydrostatic head on gas strata to prevent them from blowing out; to release entrained gas at the surface.

The rheologic properties of such fluids are all-important in determining the efficiency with which the last two functions will be performed. Before considering these functions in detail, the general properties of a drilling fluid will be considered.

1. General properties of a drilling fluid

All drilling fluids contain gelling or thixotropic colloidal material, either clay, bentonite or some other similar material. Non-colloidal material alone does not have the necessary property of staying in suspension, but settles badly. If the solids settle from the drilling fluid when drilling is stopped, they settle around the drill-stem and cause seizing or "freezing." Settling of clay solids is prevented by the gel-forming colloids which do not allow the particles to settle in accordance with Stokes' law. The viscosity of a clay suspension is not a constant but increases as the shearing stress to which it is subjected is decreased. Both ordinary clays and bentonites possess this property as well as that of thixotropy.

As shown by Ambrose and Loomis[10] the viscosities of such fluids are dependent not only on the applied shearing stresses but upon their mechanical histories. The slow settling of clays is believed to be due to the fact that very small shearing stresses are exerted by the settling particles which are therefore opposed by a high effective viscosity. This is substantiated by the fact that agitation will release from such fluids entrained sand which does not settle when quiescent. In general, therefore, a drilling fluid may be considered as a suspension whose non-colloid particles are held in suspension by the gel-forming thixotropic colloids present.

2. Importance of viscosity control

The importance attached to control of the viscosity of rotary drilling fluids has been generally recognized, and has been thoroughly discussed in previous papers.[11] The effect of viscosity on the pump pressure is small since flow is usually turbulent, with the result that the pressure varies with the 0.2 power of the viscosity. The carrying capacity for cuttings is effected by the viscosity of the fluid but is not of particular importance. Water has been satisfactorily used in rotary drilling, and has sufficient carrying capacity in spite of its low viscosity.

The viscosity of a drilling fluid is of importance in determining the ease with which it releases cuttings and entrained gas when flowing through the "mud-pits" at the surface. In accordance with Stokes' law, it is desirable that the fluid have a low viscosity in order that it may readily release cuttings and gas. The release of cuttings is necessary to prevent "freezing" of the drill stem due to cuttings settling around it when drilling is stopped. Release of gas is most desirable in order to prevent a "blow-out," for entrained gas bubbles lower the specific gravity of the fluid and therefore the hydrostatic head that it furnishes against the gas strata.

The chemical control of the viscosity of clay drilling fluids for the proper release of cuttings has been investigated by Lawton *et al.*[11] and has been successfully used in practice. Chemicals containing tannic acid and caustic soda will release particles larger than 325-mesh while retaining in suspension those smaller than this size. Chemical methods of control and reclamation of rotary drilling fluids are thought to be as effective and much more economical than mechanical methods,[12] such as thickeners, classifiers and vibrating screens.[13]

3. Thixotropic properties

In addition to lowering the viscosities of clay drilling fluids, chemicals are intended to promote the formation of a light gel, preventing settling

[10] Ambrose and Loomis, Physics **4**, 8, 267 (1933).

[11] Lawton, Ambrose and Loomis, Physics **3**, 4, 185 (1932); **3**, 5, 365 (1932).

[12] Decker, Oil and Gas J. **29** (4) 32 (1930).

[13] Marsh, Oil and Gas J. **29** (22); 92 (1930).

of sand and cuttings when the fluids are at rest in the well.

Bentonite, because of its marked thixotropic properties, is extensively employed for stabilizing the weighting materials used in drilling fluids for restraining high pressure gas. As an example, a suspension of amorphous silica of density 1.44 settles 40 percent of its solids in 24 hours.[14] The addition of 4 percent by weight of bentonite will prevent all settling during the same period, although such addition does not greatly decrease the apparent fluidity of the liquid. Its static fluidity is low, however, and it is somewhat plastic in its properties. The settling of the non-colloidal particles is prevented because of the low shearing stresses exerted by them upon the medium made plastic by the dispersion of bentonite.

The release of cuttings and gas is opposed by increasing the thixotropy of a drilling fluid. In practice it is desirable to maintain motion just short of turbulent in the "mud-pits" in order that the effective fluidity may be as high as possible. The weighting materials commonly used, barytes, silica, and iron oxide, require the presence of a thixotropic substance such as bentonite to hold them in suspension, so that the proper mechanical measures are necessary for release of cuttings and gas.

4. The viscosities of rotary drilling fluids

Although it has been recognized for a considerable time that the viscosity relations of rotary drilling fluids are of some practical importance, no method has been devised for determining viscosities applicable to flow formulae. The reason for this failure lies in the lack of uniqueness in the properties of such fluids. It has been found difficult to check measured viscosities, even with the same instrument, and there has been considerable confusion regarding the meaning of the measured values.

This confusion is somewhat cleared when it is understood that the viscosity of such a fluid is not a constant, but that it varies with the conditions under which it is measured. Therefore a standard practice of measurement is desirable with a thorough understanding of the meaning and limitations of the measured value.

[14] Ambrose and Loomis, Physics **1**, 2, 135 (1931).

5. The Stormer viscometer

The Stormer viscometer has come into wide use for determining the relative viscosities of rotary drilling fluids. The instrument contains baffle plates, causing local turbulence, so that no absolute measure of viscosity can be made. The Stormer is commonly calibrated with several driving weights, by using liquids of known viscosities, such as oils or glycerine solutions. Calibration curves are plotted for variation of the rate of revolution of the inner cup with viscosity for the different driving weights.

In measuring the relative viscosities of rotary drilling fluids, the rates of revolution are measured for several weights, and the curve of apparent viscosity for each weight *vs.* r. p. s. is interpolated to 10 r. p. s.;[14] at this speed the curves become nearly parallel and asymptotic. Although the values thus measured cannot be applied to actual flow formulae, they are very useful in the comparison of drilling fluids, and the effects of chemicals on their properties. The method is, of course, a measurement of relative viscosities at constant rate of shear. The peculiar minima found by Craft and Exner[15] in measuring the variation of viscosity with temperature do not appear when measurements are made at constant rate of shear.

A particular difficulty connected with the Stormer viscometer is that it must be calibrated often; wear or dirt in the bearings will cause large errors in its measurements.

6. Attempts to use flow formulae

Herrick,[16] considering clay suspensions as plastic solids, has attempted to devise a formula for the flow of drilling fluid through pipe by incorporating plastometer measurements of viscosity in Williams' and Hazen's formula for hydraulic flow. The measurements were made with a single capillary tube, and the results calculated to give the yield value and the "viscosity." The derivation of his formulae for viscosity is not clear, but its form is similar to that given by Bingham[17] for the mobility and

[15] Craft and Exner, A. I. M. E., Petr. Dev. and Techn. 112 (1933).

[16] Herrick, A. I. M. E., Petr. Dev. and Techn. 476 (1932).

[17] Bingham, *Fluidity and Plasticity*, McGraw-Hill Book Co., N. Y. 225 (1922).

friction of plastic materials. The mobility, (reciprocal of Herrick's viscosity) is assumed to be a constant, independent of the radius of the tube, but Bingham's data show a regular variation with increasing radius. The friction factor of a single material is also assumed to be a constant, but shows wide variations in its measured values. It appears that the data are applicable only to the instrument in which they are measured, and that they are not applicable to large scale pipes as Herrick has postulated. This conclusion is substantiated by the data of Ambrose and Loomis[10] on the flow of bentonite suspensions.

Herrick's modification of the Williams' and Hazen's formula, for a 70 lb./cu.ft. drilling fluid is as follows

$$Q = 1.24 D^{2.63}(P - 33.3/D)^{0.54},$$

where: Q = flow in gal./min.,
D = inside diameter of pipe—inches,
P = pressure drop/1000 ft.—lbs./in.^{2}.

The factor 1.24 is a modification of the Williams' and Hazen's experimental coefficient C obtained by the use of Herrick's viscosity measurements. The method of modification is not described, but the coefficient C for water varies between 105 and 170[18] for various types of pipe, as experimentally determined.

The term $33.3/D$ in the above formula is to correct the pressure by subtracting the yield value. The validity of such an equation is doubtful, especially since no actual flow data are given in substantiation.

7. Fluidities—absolute measurements

Ambrose and Loomis[10] have compared the flow characteristics of a single fluid, as measured in capillaries, brass pipes, and an absolute consistometer. The fluid, five percent bentonite in water, is typical of modern drilling fluids, but shows the property of thixotropy to a more marked degree. It is shown that equilibrium conditions of flow, that is, a dynamic equilibrium between the formation and the breakdown of a thixotropic gel, is difficult to obtain except under conditions of long time flow, and is not attained in the usual type of viscometer, such as capillary tubes or pipe. A rotary viscometer of special design was used for measuring fluidities of gels which showed reversible gellation. Thirty minutes to an hour of continuous flow at constant rate of shear were necessary before the fluidities attained a constant value. The measured fluidity increased or decreased to a constant value according to the previous history of the fluid. If it had been subjected to higher rates of shear than existed in the consistometer, its measured fluidity decreased to a constant value, or if its gel had not been sufficiently broken before measurement, the fluidity increased to a constant value.

Measurements were made with three combinations of radii for the inner and outer cups of the viscometer, as suggested by Mooney[19] for determining slippage. No slippage was found and the equation for the fluidity of suspensions of this type was found to be:

$$\varphi = m s^{n-1}$$

where: m, n = constants for the fluid,
φ = fluidity = 1/viscosity,
s = shearing stress at radius r.

The corresponding equation for tube or pipe flow was calculated as:

$$E/\pi R^3 = m S^n/(n+3)$$

E = efflux in cm^3/sec.,
R = radius of tube,
S = shearing stress at wall of tube.

This equation is similar to that of Porter and Farrow, as shown by Hatschek.[20]

The agreement between measurements in capillaries and the rotary viscometer is shown in Hatschek's comparison of the data of Couette with those of Farrow, Lowe and Neale[21] on starch paste. Starch pastes are, however, not very pronounced in their thixotropic properties, and rapidly reach a state of equilibrium flow. Further investigation of the flow of rotary drilling fluids is necessary in determining the accuracy which may be obtained by the application of rotary viscometer measurements to pipe flow. It has been shown that the true fluidities

[18] Daugherty, *Hydraulics*, McGraw-Hill Book Co., N. Y., 119 (1925).

[19] Mooney, J. Rheology **2**, 210 (1931).

[20] Hatschek, *The Viscosity of Liquids*, G. Bell and Sons, London, 217 (1928).

[21] Hatschek, *The Viscosity of Liquids*, G. Bell and Sons, London, pp. 220–221.

of five percent bentonite gel cannot be used in computing viscous pipe line flow because of the indeterminate factor introduced by their thixotropic character, (i.e., whether or not flow is under equilibrium conditions).

Further data by the authors on the flow of bentonite suspensions through brass pipes confirm Gregory's data[22] on the flow of clay suspensions through pipe lines, i.e., that these fluids behave the same in the turbulent region as any viscous liquid, and that for practical engineering purposes their flow may be assumed to be the same as that of water, allowing the use of the usual hydraulic formulae. The critical velocities of such fluids have not been determined so that the velocities at which turbulence begins in the light of present knowledge is indeterminate except by experiment.

IV. Production of Oil Through Tubing

A flowing oil well presents a peculiar and difficult problem for calculation of the pressure in the tubing or flow string of pipe. The problem is of particular importance in the proper design of tubing for the most efficient production.

A tubing string reaches to, or nearly to, the oil-producing horizon. The oil may enter the tubing with or without gas, and with or without water. Gas is released from the oil as the pressure is lowered in its ascent through the tubing. Neglecting the possibility of the presence of water, there are four general conditions in which the oil may exist in the tubing:

1. As gas-free oil.
2. As oil containing gas bubbles.
3. As a heterogeneous foam of gas and oil.
4. As a mist of oil droplets in a stream of gas.

Besides changes in the mechanical character of the fluid mixture there are several other factors involved:

1. Compressibility of gas-free oil.
2. Cooling of fluid due to expansion of gas and colder upper tubing.
3. Change of density of oil due to loss of dissolved gas.
4. Change of density of gas due to cooling and expansion.
5. Slippage of gas past the liquid.

Therefore the fluid is undergoing continuous change in its physical character throughout its travel up the tubing. The variables are so many, not only from one oil field to another, but from well to well, that a satisfactory theoretical formula for pressure drop is difficult to devise. Data on the solubility of natural gas in crude oil are not yet sufficient to offer a basis for calculation. The composition of the gas not only varies from one oil field to another, but in a single well, as the oil-gas mixture flows up the tubing.

Some success in estimating the pressure drop in tubing has been obtained by the development of empirical formulae from data taken on a number of wells.[23] We believe that further development of this problem will best be accomplished by extensive examination of carefully collected field data.

An excellent introduction to this problem may be obtained from a number of early papers on the subject.[24] Other important papers by Versluys,[25] Moore and Wilde,[26] Vietti,[27] Davis,[28] Boatright,[29] Hawkins,[30] Nowels,[31] should also be consulted.

V. The Flow of Oil in Pipe Lines

Still another phase of the petroleum industry which requires a knowledge of rheological science is the flow of oil in pipe lines. Pipe lines operate at sufficient pressure so that no gas is evolved. For oils of low pour point (under about 20°F), and for almost all oils at summer temperatures, the problem reduces to the ordinary case of the transport of viscous fluids through pipes. This can be handled by Fanning's formula, or graphically by plotting friction factor against the Reynolds number, and is amply covered in numerous treatises.

Calculation of flow, however, is much more difficult when dealing with oils containing large quantities of wax, such as East Texas and some

[22] Gregory, Mech. Eng. **49**, 609 (1927).

[23] Moore and Schilthuis, A. I. M. E. Petr. Dev. and Tech. 170 (1933).

[24] A. I. M. E., Petr. Dev. and Techn. 1930, Chap. IV, p. 192.

[25] Versluys, A. I. M. E., Petr. Dev. and Techn., 279 (1931).

[26] Moore and Wilde, A. I. M. E., Petr. Dev. and Techn., 296 (1931).

[27] Vietti, A. I. M. E., Petr. Dev. and Techn., 215 (1931).

[28] Davis, A. I. M. E., Petr. Dev. and Techn., 221 (1931).

[29] Boatright, A. I. M. E., Petr. Dev. and Techn. 295 (1932).

[30] Hawkins, A. I. M. E., Petr. Dev. and Techn., 306 (1932).

[31] Nowels A. I. M. E. Petr. Dev. and Techn., 401 (1932).

West Texas crudes, under low temperature conditions. One difficulty lies in the assignment of a value to the viscosity, which enters Fanning's formula as a fifth root. While one might assume that no great error would be introduced in the result by assigning values obtained by different methods of measurement, the reverse is seen to be the case when it is realized that viscosities, measured by different methods on a material of this kind range from quite low figures up to infinity. It is sometimes assumed that oils cannot be made to flow at temperatures below the pour point, and this is true if only low pressures are available, and if the oil is allowed to assume a gel structure before the pressure is applied.

In addition to the aspects of pipe-line flow here dealt with, especially in cold weather, is the phenomenon of the separation of wax on the walls of the pipe. The effect of this separation is to decrease the effective diameter of the pipe, and to increase the apparent viscosity of the oil, if calculations are made without taking this factor into account. In practice, this growth of wax requires the frequent running of scrapers for its removal. As this problem depends largely on factors other than the rheological properties of the oil, it cannot be dealt with further in this paper.

A second problem which is of extreme importance in pipeline operation is the determination of the pressure necessary to start flow in a line, after the flow of a gelling oil has been interrupted by a forced shutdown. The importance of this question is evident when it is considered that if the pump pressure is not sufficient to start the flow, it may be necessary to dig up and cut the line at numerous points, or to allow the line to be idle until warm weather returns. Either of these alternatives would involve a very large expense, or cause a shortage of petroleum products over large areas.

The assignment of a viscosity for steady flow for use in Fanning's formula evidently depends on the nature of the flow. For the flow causes a breakdown in the gel structure which is more rapid the faster and more turbulent the flow. On the other hand, the gel structure is being built up due to growth of wax crystals, and for steady flow an equilibrium is maintained which depends on the temperature and the nature of the flow, in addition to the characteristics of the oil. In turbulent pipe-line flow, however, the rate of gel formation is very slow compared to the rate at which it is broken down, and the authors have shown, in unpublished researches, that for East Texas oil at least, the viscosity approaches very closely the viscosity obtained by extrapolating to the desired temperature on an A. S. T. M. or MacCoull viscosity-temperature chart. It is probable that this method has utility as applied to other oils for pipe-line purposes. In assigning a viscosity to oils in viscous flow, it cannot safely be followed. Thus Louis, Jordachescu and Thiebault[32] find that at equilibrium for slow flow, an oil at 0°, is very plastic, whereas the present authors find that a gelling oil just after turbulent flow has no apparent plasticity, and the effective viscosity under these conditions is the same as if the wax were removed.

Regarding the gelling of quiescent oil in place in pipe lines, it may be said that each oil presents an individual problem. The previous heat-treatment is all important. Some oils gel most strongly when heated to about 115°F before cooling, others when heated to about 80°. If oils are allowed to stand at low temperatures after breaking up the gel initially formed, the gel strength gradually returns, reaching a steady value after about 48 hours which is still very much less than the strength of the quickly cooled gel. Measurements made by the authors indicate that pumping station pressures (700 pounds per square inch differential across 50 miles of 10-inch line) are sufficient to break the gel after East Texas oil has stood in the line at 32°F for several days. However, if the oil enters the line at a higher temperature and cools while quiescent, trouble in restarting flow may be experienced. In particular, if oil enters the line at 42°F, and cools to 32°F over a period of 48 hours, a gel is formed which cannot be sheared at available pressures.

VI. Acknowledgments

The authors are greatly indebted to Dr. Morris Muskat of the Gulf Research Laboratory for helpful discussion of the problem of flow through porous media and to Dr. Paul D. Foote for his interest and many suggestions.

[32] Louis, Jordacheseu and Thiebault, Physics **4**, 401 (1933).

The Alternating Stress Method for the Measurement of the Consistency of Very Stiff Materials

EUGENE C. BINGHAM[1] AND ROBERT A. STEPHENS[2]

(Received April 18, 1934)

Samples of rosin, abietic acid and pitch may be made to flow at temperatures as low as 20°C at low pressures and conveniently short periods of time, sufficient for fluidity determinations. Such a method as this one was devised in the hope of finding a much better control instrument for such materials. No evidence of plasticity was observed. The fluidity was found to be independent of the dimensions of the apparatus used. In the pressure range from 130 to 1800 g per cm² no effect of change of pressure upon the fluidity was detected. A study of the effect of changes in pressure upon the flow of plastic materials is now being made.

INTRODUCTION

THE rapid, practical methods for the measurement of the consistency of stiff materials are generally unsatisfactory. They do not render possible the quantitative determination of the consistency in absolute units of flow, they do not differentiate in any way between the different kinds of flow and therefore do not even recognize the variables in the problem. The measurements are not even qualitatively exact since with one instrument employing a certain shearing stress a given substance A may appear to be stiffer than another material B, yet when measured by means of a second instrument employing a different shearing stress, the substance B may conceivably appear stiffer than A. Such methods are used for measuring hardness, softening point, penetration, etc., which are measures of great importance.

Going from the very numerous practical methods to the more scientific methods, a long search does not yield the reward of a definitely workable absolute method. To be sure, Carl Barus[3] forced marine glue through a small tube at 20°C and obtained a viscosity of 2×10^8 poises, but his experiment extended over seven months. To keep the temperature and pressure constant over long periods of time for a single measurement is a prospect which would discourage any but the most stout-hearted investigators. Nevertheless, Heydweiller[4] measured the flow of solid menthol, Veinberg,[5] Dudetskii[6] and Pochettino[7] measured the viscosity of asphaltic materials, Segel[8] studied sealing wax, and Deeley and Parr[9] measured the flow of ice.

To avoid the obvious difficulties, Staudinger[10] and many others seek to avoid the difficulty altogether by the use of a dilute solution in the case of rubber or an elevated temperature in the case of glass.[11] If one must know the plasticity of ice, vulcanized rubber, an asphalt-sand mixture, a sodium chloride crystal, a gel or other similar materials where orientation or other changes may be of great importance, then a direct measurement becomes necessary.

Of course no moderate pressure will suffice to make glass, rosin, asphalt cement, etc., flow at room temperatures through small tubes, but since the flow is proportional to the fourth power of the radius of the tube, it is theoretically possible to obtain a perceptible flow in tubes of moderate size in a period of time which is not inconveniently long. The problem reduces to the precise measurement of very small amounts of deformation. The method has one marked advantage in that a reservoir of material is unnecessary and may be eliminated altogether thereby obviating any question as to resistance to

[1] Chemistry Department, Lafayette College, Easton, Pa.
[2] C. K. Williams & Co., Easton, Pa.
[3] Carl Barus, Phil. Mag. [5] **29**, 337 (1890).
[4] Heydweiller, Wied. Ann. **63**, 56 (1897).
[5] Veinberg, Proc. Phys. Soc. (London) **19**, 472 (1904), etc.
[6] Dudetskii, J. Russ. Phys. Chem. Soc., Phys. Pt. **45**, 519 (1914).
[7] Pochettino, Nuovo Cimento **8**, 77 (1914).
[8] Segel, Phys. Zeits. **4**, 493 (1903).
[9] Deeley and Parr, Phil. Mag. [6] **26**, 85 (1913), **27**, 153 (1914).
[10] Staudinger, Ber. **B63**, 730 (1930), etc.
[11] Washburn, Phys. Rev. **15**, 149 (1920), etc., and Lillie, Phys. Rev. **36**, 347 (1930).

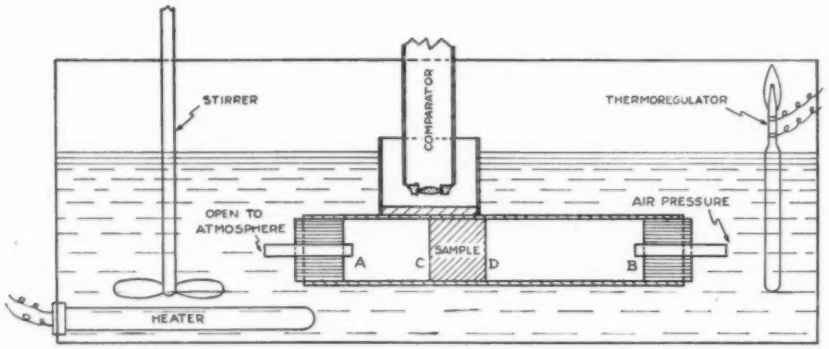

FIG. 1. Diagram of apparatus.

flow within the reservoir. There is measured then solely the deformation of a cylinder of material mounted in a glass tube to which it adheres firmly, during any convenient time and under a measured constant pressure.

THE APPARATUS AND MATERIALS

The principal feature of the apparatus is shown in Fig. 1. It consists of a glass tube *AB* closed at either end by one-hole rubber stoppers carrying glass connections to either the atmosphere or the source of constant pressure and mounted horizontally in a constant temperature bath. Within the tube there is shown at *CD* the material closely adhering to the wall of the tube and at the beginning of the measurements in the form of a true cylinder.

The flow is produced by admitting the pressure of air at one end while the other end is connected to the atmosphere. It might be measured in a variety of ways, but in this investigation a Gaertner comparator was firmly mounted from the wall of the room so as to be directly above the material in the tube. Noting the exact position of the center of the leading end at any given moment the time was measured on a stopwatch required for the material to advance any convenient distance. As soon as a measurement was completed, another measurement might be started, but preferably in the opposite direction in order to restore the cylinder to its original shape. The reason for this is that even though the material being studied is known to be a viscous liquid, nevertheless the leading and following surfaces of the two ends are not of the same shape. The leading end will be hemispherical while the following surface will have the shape of a pendant drop or nipple, Fig. 2. Since this material is continually being left behind and therefore no longer offers frictional resistance, the flow would accelerate if continued in one direction. For this reason the alternate stress method has been employed, by means of which this error may be avoided and provision made for an indefinite number of measurements upon the same material, so long as it is not changed due to chemical oxidation, to drying out or to internal structure changes affecting the orientation or aggregation of particles.

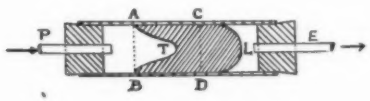

FIG. 2.

A word may be added in regard to the provision for seeing the moving material clearly, submerged as it is in a bath whose surface is continually disturbed by stirring. A circular disk of plate glass was cemented fast to a hollow cylinder of glass, the ends of which had been ground plane. Care was taken to mount the plate glass horizontally and the comparator vertically over the center of the cylinder of material with the movement of the comparator exactly parallel to the movement of the material itself. These adjustments are not difficult to make and need not be described at length.

Hercules Wood Rosin No. 1 and commercial Abietic Acid were courteously supplied for this

TABLE I. *A summary of the viscosity and the fluidity of rosin, abietic acid and pitch at various temperatures.*

Rosin		*Abietic acid*		*Pitch*	
Temp. bath °C	Ave. φ in rhes.	Temp. bath °C	Ave. φ in rhes.	Temp. bath °C	Ave. φ in rhes.
25.30	6.71×10^{-12}	20.00	1.39×10^{-12}	20.10	7.09×10^{-11}
29.80	6.67×10^{-11}	25.00	1.11×10^{-11}	25.00	3.75×10^{-10}
35.00	2.41×10^{-10}	30.10	9.43×10^{-11}	30.30	2.56×10^{-9}
45.10	9.52×10^{-9}	34.80	6.25×10^{-10}	35.00	1.20×10^{-8}
50.55	8.13×10^{-8}	40.10	5.29×10^{-9}	40.05	5.32×10^{-8}
60.00	3.97×10^{-6}	44.70	2.56×10^{-8}		
		50.00	1.79×10^{-7}		

investigation by the Hercules Powder Company. The analyses given below were furnished by Dr. Humphreys. The coal tar pitch was supplied us by the Wailes Dove Hermiston Corporation to whom acknowledgment is made. In every case care was taken to use samples which had not been exposed to the atmosphere and to avoid heating more than was necessary.

In filling the tube, which had been carefully cleaned and dried, the molten sample was poured in upon a cork plug taking care to avoid air bubbles and very slowly cooled to avoid strains. The ends of the cylinder were finally made plane by means of a specially made knife for the purpose. The inside of the cylinder was carefully cleaned.

In no case did the sample not adhere to the wall, but at first trouble was experienced due to the sample cracking due to strains on too rapid cooling. In more than one case, the strain placed upon the glass by the cooling sample was so great that the tube itself gave way. This very great adhesion of the rosin to the glass is perhaps not so remarkable as the fact that the break in the glass was everywhere continuous with the break in the rosin, showing that the two materials were actually one.

Before concluding this section, it is necessary to add that however consistency of very stiff materials is to be measured the greatest possible care must be taken in regard to the constancy of the temperature. Since the fluidity of rosin at 35° increases 37 percent for each degree Centigrade, it is obvious that to obtain an accuracy of say 0.5 percent a constancy of 0.01° would be required. Efforts were made by the use of a "metastatic" thermoregulator, rapid stirring and an adequate size of bath to obtain the necessary control for a preliminary investigation.

RESULTS

A large number of results were obtained with tubes of different radii, with different lengths of sample, with different methods of measurement as well as over a certain range of temperatures. Since the variations in length and radius were without noticeable effect upon the fluidity for the materials studied, it is perhaps sufficient to give in full merely Table I, summarizing the results for the three substances studied and as shown in Fig. 3.

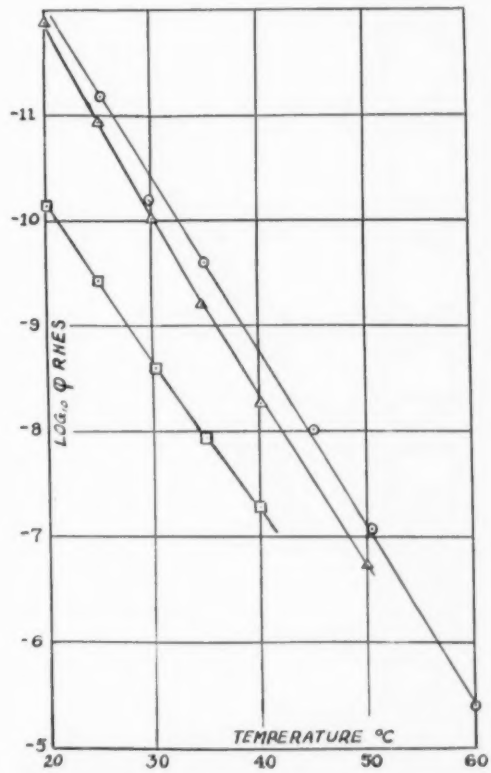

FIG. 3. Fluidity-temperature curves. Circles, Hercules No. 1 Wood Rosin; triangles, commercial abietic acid; squares, pitch.

In calculating the results, the shearing stress at the wall of the tube F bears the following relation to the pressure P upon the end of the cylinder, $F=PR/2L$. From this value of the shearing stress and the volume of flow per second, it is possible to calculate the fluidity. The materials used in this study proved to be purely viscous, therefore it has been possible to assume that the leading surface is parabolic so long as the material does not differ much from the original cylindrical form. The application of the method is being studied further but as others have made practical use of the method, it is unwise to longer delay publication.

Rheological Properties of Asphalts

I. Effect of Temperature

C. U. PITTMAN AND R. N. TRAXLER, *The Barber Asphalt Company, Maurer, N. J.*

(Received April 18, 1934)

INTRODUCTION

IN spite of the antiquity of the use of asphalts[1] little is known even at the present time concerning the chemical properties of these complex mixtures of variable composition, and it has been only within the past fifty years that any measurements have been made of their physical properties. The flow characteristics are probably among the most important of the physical properties of bitumens and mixtures containing them. Indefinite measures of the rheological properties are given by the commonly used tests such as penetration, float, softening point and ductility. When some rapid and accurate method requiring little skill to use is developed, these various tests should be replaced by measurements of the rheological properties in absolute units, except for routine control work in the field. Though this ideal has not yet been realized, methods and apparatus are available which will with proper care allow the determination of the type of flow and the calculation of viscosity or mobility and yield value of materials such as asphalts.

Twenty years ago several European investigators in their study of asphalts used rather crude methods to compare flow properties. Trouton[2, 3] working with pitch, wax and tar, and Pochettino[4] with pitch, developed methods which they used to measure the absolute viscosity of these substances. Numerous other citations of the literature might be given which deal with very viscous materials, but asphalts appear to have been rather neglected until comparatively recent times.

Recently, Saal and Koens[5] and Saal[6] studied the rheological properties of several asphalts at different temperatures. They found that some were viscous while others were either plastic solids or non-Newtonian liquids. Some of the bitumens were found to be elastic and some types to exhibit thixotropy. Mack[7] measured the relative viscosities of the petrolenes of an asphalt and mixtures of these petrolenes and various amounts of asphaltenes at different temperatures. Using a falling sphere viscometer, Broome and Thomas[8] found the asphalts which they studied to be viscous liquids.

The information that is available in the literature may seem to the casual reader to be rather contradictory as to the type of flow exhibited by asphalts. Anyone familiar with such materials knows that they are complex mixtures which are often altered by prolonged standing and usually radically changed by overheating. Further, asphalts processed in the same manner from petroleums from different sources rarely have the same physical properties; in fact, those prepared from the same petroleum can be made to differ in properties by changes in the refining procedure. For these reasons in any investigation dealing with asphalts, the source, method of processing, and some commonly measured properties should be given to aid in identifying the materials as has been pointed out by Traxler and Pittman.[9] It is to be regretted that in the papers so far published all of this information has not been given.

ASPHALTS USED

The asphalts used in this work are listed below together with information which we believe

[1] H. Abraham, *Asphalts and Allied Substances*, 3rd Ed., D. Van Nostrand Co., Inc., New York (1929).
[2] F. I. Trouton and E. Andrews, Phil. Mag. **7**, 347 (1904).
[3] F. I. Trouton, Proc. Roy. Soc. London **A77**, 426 (1906).
[4] A. Pochettino, Nuovo cimento **8**, 77 (1914).
[5] R. N. J. Saal and G. Koens, J. Inst. Petroleum Tech. **19**, 176 (1933).
[6] R. N. J. Saal, *Determinations Regarding the Plastic Properties of Asphaltic Bitumens*. Preprint 96, World Petroleum Congress at London, England, July 1933.
[7] C. Mack, J. Phys. Chem. **36**, 2901 (1932).
[8] D. C. Broome and A. R. Thomas, J. Soc. Chem. Ind. **50**, 424T (1931).
[9] R. N. Traxler and C. U. Pittman, Chem. and Ind. **52**, 221 (1933).

should identify them. The data given on penetration, float, softening point, and ductility were obtained using A.S.T.M. apparatus and procedures.

Asphalt *A*

Produced from Mexican Petroleum by steam distillation in a batch still.
Penetration at 25°C (77°F) 100/5 62
Ring and Ball Softening Point . . . . . 52.2°C (126°F)
Ductility at 25°C (77°F) . . . 100 cm +

Asphalt *B*

Produced from Venezuelan Petroleum from the Mene Grande field by steam distillation in a batch still.
Penetration at 25°C (77°F) 100/5 61
Ring and Ball Softening Point . . . . . 52.2°C (126°F)
Ductility at 25°C (77°F) . . . 100 cm +

Asphalt *C*

Produced from petroleum from the Island of Trinidad by steam distillation in a batch still.
Penetration at 25°C (77°F) 100/5 60
Ring and Ball Softening Point . . . . . 47.8°C (118°F)
Ductility at 25°C (77°F) . . . 100 cm +

Asphalt *D*

Refined Bermudez Native Lake Asphalt softened with an asphaltic flux of 45 seconds float at 65.6°C (150°F) produced by steam distillation of petroleum used in production of Asphalt B.
Penetration at 25°C (77°F) 100/5 61
Ring and Ball Softening Point . . . . . 50.0°C (122°F)
Ductility at 25°C (77°F) . . . 71 cm

Asphalt *E*

Refined Trinidad Native Lake Asphalt softened with the same flux as used in making Asphalt D.
Penetration at 25°C (77°F) 100/5 62
Ring and Ball Softening Point . . . . . 51.7°C (125°F)
Ductility at 25°C (77°F) . . . 85 cm

Asphalt *F*

Produced by air reduction from same petroleum used in making Asphalt B.
Penetration at 25°C (77°F) 100/5 60
Ring and Ball Softening Point . . . . . 64.4°C (148°F)
Ductility at 25°C (77°F) . . . 8 cm

Methods

Although there have been several methods described for measuring the flow properties of materials of high consistency, we have used the two discussed below because of their simplicity and the ease with which the necessary apparatus could be constructed.

1. Bingham-Stephens method

The method and apparatus used to measure the consistencies of asphalts over the temperature range in which the viscosities varied from 10^5 to 10^8 poises were the same as described by Bingham and Stephens.[10] A water bath, the temperature of which was maintained within ± 0.1°C, surrounded the tube. The distance of flow was measured by a cathetometer reading to 0.001 cm and the time to produce this flow by a one-fifth second stopwatch. Apparently it made no difference in the results whether the extrusion caused by the flow was being forced out or back. The radii of the tubes used were measured by internal calipers and checked by the cathetometer. The tubes varied from 1 cm to 0.14 cm in radius.

To determine the type of flow exhibited by the various asphalts at each of the temperatures, a rate of flow *vs.* shearing stress diagram was made. McLean,[11] assuming that the velocity gradient in the asphalt column is a function only of the shearing stress, showed that a plot of $2h/Rt$ *vs.* $PR/2L$,

where h = length of extrusion in cm in time t,
R = radius of tube in cm,
t = time of flow in seconds,
P = pressure applied in dynes/cm^2,
and L = length of asphalt column in cm,

[10] E. C. Bingham and R. A. Stephens, Physics **5**, 217 (1934).
[11] D. A. McLean, private communication.

for a given material is independent of R and L if no radial flow occurs. With such a plot a straight line through the origin indicates viscous flow; a curved line through the origin, flow of a non-Newtonian liquid; and a curve with an intercept on the shearing stress-axis, plastic flow. To calculate the viscosity of a Newtonian liquid the following equation may be used:

$$\eta = PR^2t/4hL.$$

With this apparatus, assuming that no radial flow takes place, the cumulative errors in a single observation should not exceed ± 5 percent. Of course, the error in any value given in Table I will be much less because of the number of determinations made.

2. A tube method based on the Bingham-Murray plastometer

For measurements at temperatures where the viscosities were of the order 5 to 10^5 poises a method based on that of Bingham and Murray[12] was used. Numerous experiments were first made with an apparatus similar to the modification described by Gregory, Rassweiler and Lampert[13] in which the capillaries in their arrangement were replaced with tubes of larger radii and the vacuum with a pressure system. However, the bend in the tube caused appreciable errors in the rate of flow, so the method was abandoned, and the apparatus shown in Fig. 1 was then constructed. It consisted of a small aspirator bottle which served as a reservoir, glass tubes of uniform radii, and a source of constant pressure. A tube was passed through a cork stopper in the side opening and extended to the center of the bottle. A piece of glass tubing through the stopper in the top opening connected the bottle to the air pressure, and a three-way stopcock was so placed that the pressure on the bottle could be quickly released. The tube, the ends of which were ground square, was levelled and clamped firmly against a support carrying a millimeter scale. The temperature of the air bath in which the apparatus was set up was controlled by a thermoregulator to ± 0.1°C at the lower, and to ± 0.3°C at the higher temperatures where the effect of temperature was much less. The lengths of the tubes, which were about 60 cm, were measured to within a millimeter. To determine the radii of all except the largest size, an oil of known viscosity from the Bureau of Standards and the method of calibration described by Gregory, Rassweiler and Lampert[13] were used. All of the tubes, which varied in radius from 0.3 to 0.03 cm were carefully selected and were found to be quite uniform, so the same radius was used for the whole length.

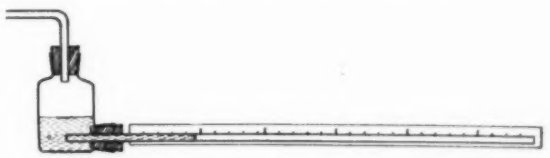

FIG. 1. Diagram of apparatus.

After the asphalt had reached the desired temperature, pressure was applied causing the material to flow into the tube. To avoid as much as possible the influence of end-effects, the asphalt was allowed to flow some distance before measurements were begun. The time t necessary to flow through a given length of tube d under the known pressure P was measured by a one-fifth second stop watch; then the pressure was changed and the procedure repeated. It can be seen that the length of the column of asphalt L being sheared varied, so the length for each measurement was taken as the distance from the end of the tube at which the asphalt entered to the point midway between the place where flow started and stopped.

Assuming that no end-effect exists and that the velocity gradient is a function only of the shearing stress, a plot of $4d/Rt$ *vs.* $PR/2L$ gives a flow-shear diagram which is independent of L and of the radius R. The viscosity of a Newtonian liquid is then found to be:

$$\eta = PR^2t/8Ld.$$

Here again, the cumulative errors in a single observation should not exceed ± 5 percent providing no end effects exist.

DISCUSSION

Though it approached more nearly a true viscous state as the temperature was raised, air-

[12] E. C. Bingham and H. A. Murray, Jr., Proc. Am. Soc. Testing Materials **23**, II, 655 (1923).

[13] D. V. Gregory, G. M. Rassweiler and K. C. Lampert, J. Rheology **1**, 30 (1929).

TABLE I. *Viscosity-temperature data.*

Temp. °C	Viscosity in poises				
	A	*B*	*C*	*D*	*E*
15	9.20×10^{7}	6.33×10^{7}	6.489×10^{7}	3.689×10^{7}	4.323×10^{7}
20	2.257×10^{7}	1.760×10^{7}	1.472×10^{7}	—	1.245×10^{7}
21	—	—	—	9.57×10^{6}	9.49×10^{6}
25	6.98×10^{6}	6.24×10^{6}	3.347×10^{6}	3.663×10^{6}	4.059×10^{6}
30	2.753×10^{6}	1.806×10^{6}	9.024×10^{5}	1.2773×10^{6}	1.323×10^{6}
35	8.45×10^{5}	4.97×10^{5}	2.503×10^{5}	4.91×10^{5}	4.835×10^{5}
40	2.331×10^{5}	1.713×10^{5}	8.063×10^{4}	1.2755×10^{5}	1.376×10^{5}
50	4.230×10^{4}	2.412×10^{4}	1.3985×10^{4}	2.096×10^{4}	2.256×10^{4}
60	8.672×10^{3}	4.719×10^{3}	2.7336×10^{3}	4.284×10^{3}	4.823×10^{3}
70	2.266×10^{3}	1.1963×10^{3}	7.68×10^{2}	1.1887×10^{3}	1.451×10^{3}
80	7.013×10^{2}	3.591×10^{2}	2.515×10^{2}	3.714×10^{2}	4.745×10^{2}
90	2.414×10^{2}	1.323×10^{2}	7.913×10	1.4971×10^{2}	2.065×10^{2}
100	1.0250×10^{2}	5.995×10	3.347×10	6.273×10	9.102×10
110	4.3185×10	2.585×10	1.609×10	2.927×10	*
120	2.267×10	1.425×10	8.47	1.459×10	*
130	1.1318×10	6.766	4.837	8.744	*

* Not obtained due to the too rapid settling of a portion of the mineral matter which is naturally present in this asphalt.

blown asphalt *F* exhibited quasi-viscous or pseudo-plastic flow at temperatures from 15 to 130°C. This type of flow together with some degree of elasticity seem to be characteristic of all asphalts which have been subjected to appreciable air-reduction. Other data which we have obtained seem to indicate that steam-refined asphalts, appreciably harder than those discussed in this paper, possess these same characteristics but to a lesser degree than air-blown asphalts of the same penetration.

Asphalts *A*, *B*, *C*, *D* and *E* appeared to follow the law of viscous flow, but all had different temperature-viscosity coefficients for any given temperature range as can be seen from Table I. When these data were plotted, smooth curves were obtained which showed no marked discontinuities when passing from the results obtained by one method to those by the other. Each of the values shown in Table I is the average of ten or more determinations made at different shearing stresses. Average deviations for each value in the table were calculated and the number of significant figures determined with the method described by Wendell and Severinghaus;[14] the average deviation seldom exceeded two percent and in most cases was below one percent.

Because of the difficulty in interpolating a viscosity-temperature plot over a wide range, it is desirable to have an equation accurately relating temperature and viscosity. Numerous empirical equations for such a purpose have been published. Recently the American Society for Testing Materials advanced the following equation for lubricating oils:[15]

$$\log\log(\text{viscosity in centistokes}+0.8)=a+b\log T,$$

where $T=459.4+$ temperature in °F, and a and b are constants. It has been stated that this equation applies satisfactorily to viscous asphalts.[16] It was applied to the data listed in Table I and to that of Saal and Koens[5] and found to give some deviations as great as 25 to 30 percent from the experimental values. The deviations were not haphazard but appeared to pass smoothly from minima to maxima. Other empirical formulae have been used but none were of any practical value because the number of constants necessary to give deviations within the experimental error was too great to allow the equations to be used conveniently.

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[14] G. V. Wendell and W. L. Severinghaus, *Precision of Measurements and Precision Problems.* (1931).

[15] Proc. Am. Soc. Testing Materials **32**, I, 772 (1932).

[16] Oil and Gas J. **32**, June 8, 1933.